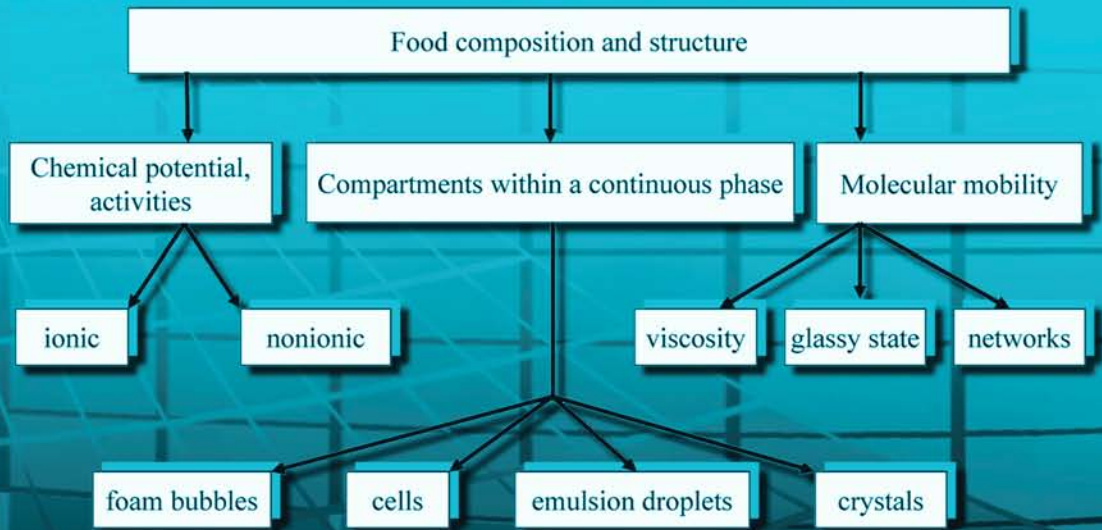


Kinetic Modeling of Reactions in Foods



Martinus A. J. S. van Boekel

Kinetic Modeling of Reactions in Foods

FOOD SCIENCE AND TECHNOLOGY

Editorial Advisory Board

- Gustavo V. Barbosa-Cánovas** Washington State University–Pullman
P. Michael Davidson University of Tennessee–Knoxville
Mark Dreher McNeil Nutritionals, New Brunswick, New Jersey
Richard W. Hartel University of Wisconsin–Madison
Lekh R. Juneja Taiyo Kagaku Company, Japan
Marcus Karel Massachusetts Institute of Technology
Ronald G. Labbe University of Massachusetts–Amherst
Daryl B. Lund University of Wisconsin–Madison
David B. Min The Ohio State University
Leo M. L. Nollet Hogeschool Gent, Belgium
Seppo Salminen University of Turku, Finland
John H. Thorngate III Allied Domecq Technical Services, Napa, California
Pieter Walstra Wageningen University, The Netherlands
John R. Whitaker University of California–Davis
Rickey Y. Yada University of Guelph, Canada

Kinetic Modeling of Reactions in Foods

Martinus A. J. S. van Boekel



CRC Press

Taylor & Francis Group

Boca Raton London New York

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

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

© 2009 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works
Printed in the United States of America on acid-free paper
10 9 8 7 6 5 4 3 2 1

International Standard Book Number-13: 978-1-57444-614-2 (Hardcover)

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

Van Boekel, Martinus A. J. S.
Kinetic modeling of reactions in foods / Martinus A. J. S. van Boekel.
p. cm. -- (Food science and technology)
"A CRC title."
Includes bibliographical references and index.
ISBN 978-1-57444-614-2 (alk. paper)
1. Food--Analysis. 2. Chemical kinetics--Mathematical models. 3. Food adulteration and inspection.
I. Title. II. Series.

TX545.V36 2008
664.001'54--dc22

2008044086

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

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

Dedication

*To my wife Corrie
For her patience and understanding*

Contents

Preface	xiii
Author	xvii
1 Kinetic View on Food Quality	1-1
1.1 Introduction	1-1
1.2 Food Quality	1-1
1.3 Foods as Complex Reaction Media	1-6
1.4 Outline of the Book	1-7
Bibliography and Suggested Further Reading	1-8

SECTION I The Basics

2 Models and Modeling	2-1
2.1 Introduction	2-1
2.2 Models and Modeling	2-1
2.3 Concluding Remarks	2-12
Bibliography and Suggested Further Reading	2-12
3 Chemical Thermodynamics in a Nutshell	3-1
3.1 Introduction	3-1
3.2 Quantification of Reactants and Products	3-1
3.3 Thermodynamics of Reactions	3-6
3.3.1 Heat and Work	3-6
3.3.2 Energy	3-8
3.3.3 Enthalpy	3-9
3.3.4 Entropy	3-11
3.3.5 Free Energy	3-15
3.3.6 Chemical Potential	3-18
3.3.7 Ideal Solutions	3-20
3.3.8 Ideal Dilute Solutions	3-21
3.3.9 Real, Nonideal Solutions: Activity Concept	3-22
3.3.10 Standard States	3-27
3.3.11 Solvent Activity and Water Activity	3-29
3.3.12 Chemical Potential and Equilibrium	3-33

3.3.13	Equilibrium Constants	3-36
3.3.14	Thermodynamic Potentials and Conjugate Variables	3-42
3.3.15	Nonequilibrium or Irreversible Thermodynamics	3-48
3.4	Concluding Remarks	3-52
Appendix 3.1 Datasets Used for Examples in This Chapter		3-53
Bibliography and Suggested Further Reading		3-57
4	Chemical Reaction Kinetics	4-1
4.1	Introduction	4-1
4.2	Foods as Chemical Reactors?	4-2
4.3	Rate and Extent of Reactions in Closed Systems	4-4
4.3.1	Kinetics of Elementary Reactions	4-9
4.3.2	Kinetics of Experimentally Observed Reactions	4-16
4.3.3	Steady-State Approximation and Rate-Controlling Steps	4-28
4.4	Catalysis	4-33
4.4.1	General Catalysis	4-33
4.4.2	Acid-Base Catalysis	4-34
4.5	Kinetics of Radical Reactions	4-37
4.6	Kinetics of Photochemical Reactions	4-41
4.7	Diffusion-Limited Reactions in Aqueous Solutions	4-42
4.8	Kinetics in Open Systems	4-46
4.9	Concluding Remarks	4-53
Appendix 4.1 Datasets Used for Examples in This Chapter		4-54
Bibliography and Suggested Further Reading		4-61
5	Temperature and Pressure Effects	5-1
5.1	Introduction	5-1
5.2	van't Hoff Equation	5-1
5.3	Transition State Theory	5-3
5.4	Arrhenius' Law	5-8
5.5	Empirical Relations to Describe Temperature Dependence	5-15
5.6	Activation Energy and Catalysis	5-16
5.7	Parameters Used in Food Science	5-18
5.8	Enthalpy/Entropy Compensation	5-21
5.9	Variable Temperature Kinetics	5-23
5.10	Effect of Pressure	5-32
5.11	Concluding Remarks	5-36
Appendix 5.1 Datasets Used for Examples in This Chapter		5-36
Bibliography and Suggested Further Reading		5-41
6	Charge Effects	6-1
6.1	Introduction	6-1
6.2	Models for Ion Activities	6-1
6.2.1	Debye-Hückel Type Models	6-4
6.2.2	Mean Spherical Approximation Theory	6-8
6.2.3	Pitzer Equations	6-11

6.3	Ion Pairing Models	6-12
6.3.1	Mass Action Law	6-15
6.3.2	Pytkowicz Model.....	6-18
6.3.3	Binding MSA Model	6-23
6.4	Kinetics of Reactions between Ions	6-25
6.4.1	Primary Salt Effect.....	6-25
6.4.2	Secondary Salt Effect.....	6-29
6.4.3	Examples Showing the Primary Salt Effect on Kinetics	6-31
6.5	Concluding Remarks	6-40
	Appendix 6.1 Datasets Used for Examples in This Chapter.....	6-40
	Bibliography and Suggested Further Reading.....	6-46
7	Kinetics and Statistics	7-1
7.1	Introduction	7-1
7.2	Some Background on Statistical Approaches	7-2
7.2.1	Classical Sampling Theory.....	7-3
7.2.2	Maximum Likelihood	7-3
7.2.3	Bayesian Statistics	7-4
7.2.4	Resampling Methods	7-7
7.3	Experimental Design: Statement of the Problem.....	7-9
7.4	On Errors and Residuals	7-13
7.4.1	Deterministic and Stochastic Models	7-13
7.4.2	Least Squares Regression	7-14
7.4.3	Sums of Squares and ANOVA	7-15
7.4.4	Error Structure of Data: A Variance Model	7-16
7.5	Linear and Nonlinear Models	7-20
7.6	A Closer Look at Assumptions for Parameter Estimation	7-21
7.7	Normal Probability Plots and Lag Plots	7-25
7.8	Goodness of Fit and Model Discrimination	7-29
7.9	Precision of Regression Lines and Parameter Estimates	7-40
7.9.1	Jackknife Method	7-50
7.9.2	Bootstrap Method	7-50
7.9.3	Grid Search Method.....	7-53
7.9.4	Monte Carlo Method	7-57
7.9.5	Bayesian Analysis Using Markov Chain Monte Carlo Methods	7-57
7.10	Variability and Uncertainty	7-64
7.11	Transformation of Parameters: Reparameterization	7-68
7.12	Propagation of Errors	7-72
7.13	Sensitivity Analysis	7-74
7.14	Experimental Design	7-76
7.14.1	Systematic and Random Errors: Accuracy and Precision	7-77
7.14.2	Experimental Design for Kinetic Models	7-78
7.15	Concluding Remarks	7-87
	Appendix 7.1 Datasets Used for Examples in This Chapter.....	7-87
	Bibliography and Suggested Further Reading.....	7-94

SECTION II Application of the Basics to Chemical, Biochemical, Physical, and Microbial Changes in the Food Matrix

8	Multiresponse Kinetic Modeling of Chemical Reactions	8-1
8.1	Introduction	8-1
8.2	What Is Multiresponse Modeling?	8-1
8.3	Determinant Criterion	8-3
8.4	Model Discrimination and Goodness of Fit for Multiresponse Models	8-5
8.5	Examples of Multiresponse Modeling of Reactions in Foods.....	8-7
8.5.1	Heat-Induced Acid Hydrolysis of Sucrose	8-7
8.5.2	Degradation of Chlorophyll	8-8
8.5.3	Aspartame Degradation	8-16
8.5.4	Maillard Reaction	8-19
8.6	Concluding Remarks	8-26
	Appendix 8.1 Datasets Used for Examples in This Chapter	8-27
	Bibliography and Suggested Further Reading	8-29
9	Enzyme Kinetics	9-1
9.1	Introduction	9-1
9.2	Michaelis–Menten Kinetics	9-4
9.2.1	Linearized Plots	9-13
9.3	Enzyme Inhibition	9-16
9.4	Progress Curves	9-20
9.5	Kinetics of Two-Substrate Reactions	9-29
9.6	Other Types of Enzyme Kinetics	9-32
9.7	Temperature Effects	9-36
9.8	pH Effects	9-39
9.9	Experimental Design for Enzyme Kinetics	9-42
9.10	Enzyme Kinetics in Foods	9-43
9.11	Concluding Remarks	9-47
	Appendix 9.1 Datasets Used for Examples in This Chapter	9-48
	Bibliography and Suggested Further Reading	9-58
10	Kinetics of Protein and Enzyme Denaturation	10-1
10.1	Introduction	10-1
10.2	Protein Stability	10-1
10.3	General Kinetic Schemes Describing Enzyme Inactivation	10-13
10.4	Food Matrix Effects	10-26
10.5	Concluding Remarks	10-29
	Appendix 10.1 Datasets Used for Examples in This Chapter	10-29
	Bibliography and Suggested Further Reading	10-36
11	Kinetics of Physical Changes	11-1
11.1	Introduction	11-1
11.2	Kinetics of Diffusion	11-2
11.2.1	Fick's Laws	11-2
11.2.2	Maxwell–Stefan Approach	11-8

11.3	Kinetics of Changes in Dispersity	11-14
11.3.1	Kinetics of Aggregation of Colloids	11-14
11.3.2	Kinetics of Creaming or Settling	11-19
11.3.3	Kinetics of Coalescence	11-21
11.3.4	Kinetics of Ostwald Ripening	11-23
11.3.5	Kinetics of Gelation of Particles	11-24
11.3.6	Kinetics of Crystallization	11-28
11.4	Kinetics of Texture Changes	11-29
11.5	Partitioning Phenomena	11-32
11.5.1	Partition Coefficients	11-33
11.5.2	Partitioning of Volatiles	11-33
11.5.3	Partitioning of Weak Acids	11-46
11.6	Concluding Remarks	11-49
Appendix 11.1	Datasets Used for Examples in This Chapter	11-49
	Bibliography and Suggested Further Reading.....	11-59
12	Kinetics of Microbial Growth	12-1
12.1	Introduction	12-1
12.2	Primary Growth Models	12-2
12.2.1	Differential Equations	12-3
12.2.2	Algebraic Equations	12-6
12.3	Secondary Models	12-11
12.4	Nonisothermal Growth Modeling	12-20
12.5	Bayesian Modeling	12-22
12.6	Experimental Design	12-28
12.7	Effects of the Food Matrix	12-28
12.8	Concluding Remarks	12-29
Appendix 12.1	Datasets Used for Examples in This Chapter	12-30
	Bibliography and Suggested Further Reading.....	12-40
13	Kinetics of Inactivation of Microorganisms	13-1
13.1	Introduction	13-1
13.2	Kinetics of Inactivation of Vegetative Cells	13-1
13.3	Kinetics of Inactivation of Spores	13-10
13.4	Temperature Dependence of Microbial Inactivation	13-16
13.5	Food Matrix Effects	13-24
13.6	Concluding Remarks	13-26
Appendix 13.1	Datasets Used for Examples in This Chapter	13-26
	Bibliography and Suggested Further Reading.....	13-42
14	Modeling the Food Matrix	14-1
14.1	Introduction	14-1
14.2	Specific Effects in Aqueous Solutions	14-3
14.2.1	Water Activity and the Effect of Cosolutes	14-4
14.2.2	Water Activity and Food Stability	14-11
14.2.3	Ionic and Nonionic Solute Interactions	14-14
14.2.4	Significance of pH in Food	14-18
14.3	Transport Phenomena and Molecular Mobility in the Food Matrix	14-23
14.4	Micellar Effects	14-32

14.5	Effect of Molecular Crowding in the Food Matrix	14-34
14.6	Concluding Remarks	14-36
Appendix 14.1	Datasets Used for Examples in This Chapter	14-37
	Bibliography and Suggested Further Reading	14-53
15	Retrospective and Outlook	15-1
15.1	Introduction	15-1
15.2	Shelf Life Modeling as an Integrative Approach	15-1
15.2.1	Shelf Life from the Product Point of View	15-2
15.2.2	Shelf Life from the Consumer Point of View	15-4
15.3	Some Developments	15-12
15.4	Concluding Remarks	15-14
Appendix 15.1	Datasets Used for Examples in This Chapter	15-15
	Bibliography and Suggested Further Reading	15-19
Appendix A	Some Calculus Rules	A-1
Appendix B	Ways to Express Amounts of Reactants and Products	B-1
Appendix C	Interconversion of Activity Coefficients Based on Mole Fractions, Molalities, and Molarities	C-1
Appendix D	Differential and Integrated Rate Equations for Kinetic Models of Complex Reactions	D-1
Appendix E	McMillan–Mayer and Lewis–Randall Framework and Equations for the Mean Spherical Approximation Theory	E-1
Appendix F	Probability Laws and Probability Models	F-1
Appendix G	Use of Matrix Notation in Model Representation and Regression Analysis	G-1
Appendix H	Some Thermodynamic Activity Coefficient Models	H-1
Appendix I	Reliability Engineering and the Weibull Model	I-1
	List of Symbols and Units	16-1
	Index	I-1

Preface

The topic of food quality is receiving ever-increasing attention. Consumers are concerned about the quality of their food and have high demands. At the same time, consumer demands are rapidly changing, and the food supply chain needs to match these changing demands in order to be able to deliver food of a desired quality at the end of the chain. However, the quality of a food changes continuously along its way through the food chain. It is therefore important to have tools to control and predict food quality (including food safety) and to be able to quickly change food design according to changing consumer expectations. This is useful for consumers because it helps to ensure that their needs are fulfilled and that they obtain safe food. Obviously, it is helpful for the food industry because it provides a suitable tool to connect physical product properties with consumer wishes. I am convinced that the use of mathematical models for modeling of quality attributes of foods is going to be of great help in these matters.

This book is about how to model changes taking place in foods, for which the scientific term is kinetics. The aim of this book is to introduce appropriate kinetic models and modeling techniques that can be applied in food science and technology. It is fair to say that mathematical modeling is already used to some extent in the food science and technology world, but in the author's opinion there are many more opportunities than those currently applied. This book aims to indicate directions for the use of modeling techniques in food science. It will be argued that modeling of food quality changes is in fact kinetic modeling. However, this is not just another book on kinetics. Rather, it integrates food science knowledge, kinetics, and statistics, so as to open the possibility to predict and control food quality attributes using computer models. Moreover, much more information can be extracted from experiments when quantitative models are used. I hope to show with this book that the quality of modeling can be improved considerably with proper mathematical and, especially, statistical techniques.

The choice of topics reflects my research interests. Obviously, this choice is subjective and reflects my ideas about how modeling of food quality should be done. Quality changes in foods are related to the chemical, biochemical, physical, and microbiological changes taking place in the food, in relation to processing conditions. I have attempted to apply kinetic models using general chemical, physical, and biochemical principles, but allowing for typical food-related problems. The general principles mentioned are usually derived for only very simple, dilute, and ideal systems. Foods are all but simple, ideal, and dilute. Another important point in my view is that allowance should be made for variability and uncertainty, and therefore I consider the use of statistics as indispensable. A substantial part of this book is devoted to the use of statistical techniques in kinetic modeling, which is another reason it is not a typical kinetics book. I introduce the concept of Bayesian statistics, which is hardly known in the food science world. I feel it has great potential, and I intend to show that in this book.

The book is first of all meant for food scientists who want to learn more about modeling. It was written with two objectives in mind. The first was to introduce the topic of kinetics and its application to foods to students and graduates in food science and technology. I teach kinetics to food science students in an advanced MSc course called "Predicting Food Quality" and in an advanced PhD course called "Reaction Kinetics in Food Science" at Wageningen University. The response of the students is encouraging.

The book could therefore be helpful as a textbook in advanced MSc and PhD courses at other universities. The second objective was to write a reference book to be used by professional researchers active in food-related work. It should be useful, therefore, for graduates working in the food industry who have a keen interest in modeling, and who are willing to apply modeling concepts in food product design. It could even be useful for nonfood disciplines such as biotechnology, pharmacy, nutrition, and general biology and chemistry. It is on an advanced level in the sense that it builds upon basic food science and technology knowledge, as well as basic mathematical knowledge of calculus and matrix algebra. Also, basic statistical knowledge is assumed, although some introduction is given to Bayesian statistics because this will be new to most food scientists. As a reminder for the reader, appendices consisting of the basic background on all these matters are provided. The ultimate aim is to guide students, graduates, and postgraduates in such a way that they can understand and critically read articles in the literature concerning this topic, and can apply the principles in their own research, be it fundamental or applied.

It is, of course, unavoidable that there are many equations in this book since it deals with mathematical models. Fortunately, mathematical complexity can be kept to a minimum using appropriate software such as Mathematica, MathCad, Maple, and even well-known spreadsheets such as Microsoft Excel. I used MathCad and Excel quite extensively for this book, as well as some specialized software where indicated. The reader should try to look beyond the equations and math involved and it will be very helpful to work out the examples given. Wherever possible, I will express in words also what is expressed in an equation. Nevertheless, I do realize that the many mathematical and statistical equations are not easy to digest. Therefore, I have strived to illustrate the concepts introduced with many real-life examples rather than using hypothetical data, or examples that are less relevant for food science problems. The data for the examples were either read directly from tables published in papers, or digitally scanned by computer from graphs. Occasionally, authors supplied me with data, for which I am very grateful, and I also used my own data. All datasets used are supplied in appendices to the chapters, including their sources, so that the interested reader can work with these examples by himself or herself. I would like to stress that the examples chosen are not meant to criticize results; they are chosen because they illustrate the points I want to make. I am actually quite grateful that authors made it possible to extract data from the publications; this is actually as it should be.

I have used many references from literature in compiling my own text, by going well beyond the food science and technology literature. However, I decided not to indicate literary references in the text itself to improve readability. Rather, whenever substantial use was made of a particular reference that reference was mentioned at the end of the chapter. I do acknowledge all the excellent articles that are available and which substantially helped me to formulate my own text.

Finally, I would like to acknowledge several persons who have been instrumental in helping me realize this book. First of all, I would like to acknowledge Professor Dr. Bronek Wedzicha from the Procter Department of Food Science, University of Leeds, United Kingdom. Thanks to his hospitality, I have been able to spend two sabbatical periods of three months at the University of Leeds in the summers of 1999 and 2004 and during these periods we had very intensive discussions over the topics covered in this book. Moreover, he and his wife Glenis have been very generous to me on a personal level by inviting me to many lovely dinners at their house, and for entertaining walks in beautiful Yorkshire. I do regret not having Professor Wedzicha as a coauthor; the book would have been much better had this been the case. However, his critical spirit has been essential for my writing and many of his thoughts are reflected in this book. This is especially true for Chapter 14, which has been inspired strongly by his ideas and lectures on this topic. Furthermore, I would like to thank Professor Pieter Walstra from Wageningen University for stimulating me to take this path in my academic career, and for critically reading several drafts of the chapters. I would also like to thank Professor Willem Norde from Wageningen University for very useful comments on the chapter on thermodynamics. Having acknowledged Bronek Wedzicha, Pieter Walstra, and Willem Norde for their invaluable contributions, I am of course fully responsible for the text,

including all errors and mistakes. I would very much appreciate remarks, criticism, and corrections from readers. Last but not least, I would like to take this opportunity to thank my wife Corrie for being very patient with me, for not complaining about my physical absence of two periods of three months abroad, not to mention the countless evening and weekend hours, just so that I could do my writing. It is well appreciated and I dedicate this book to her.

M.A.J.S. (Tiny) van Boekel
Wageningen

Author



Martinus van Boekel received his BSc, MSc, and PhD in food science and technology from Wageningen University, Wageningen, the Netherlands. Immediately after, from 1980 to 1982, he worked at the Food Inspection Service at Rotterdam, the Netherlands, as a food chemist. He then returned to Wageningen University to work as an assistant professor from 1982 to 1994, as an associate professor from 1994 to 2001, and as a full professor from 2001 onward in the field of food science and technology. In 2006, he became the scientific director of the graduate school VLAG (Food, Nutrition, Agrotechnology, and Health) for 4 years. His research and teaching encompass modeling of food quality attributes in an integrative way, that is, integrating the various food science disciplines but also nutrition, marketing, economics, and quality management. He has been a visiting professor at the University of Madison, Wisconsin, and the Procter Department of Food Science, University of Leeds, United Kingdom. He is the author and coauthor of about 160 refereed scientific papers and author/editor of six books.

1

Kinetic View on Food Quality

1.1 Introduction

The aim of this book is to discuss kinetics of reactions in foods in relation to food quality. By reactions we mean all type of change taking place in the food whether they be chemical, enzymatic, physical, or microbial. Kinetics is about change. For the moment it suffices to describe kinetics as the translation of knowledge (theoretical as well observational) on a time-dependent chemical, physical, microbial, reaction into an equation describing such changes in mathematical language. The mathematical relations result in models that we can use to design, optimize, and predict the quality of foods. It should also be helpful in choosing the technology to produce them. We thus need chemical, physical, microbial knowledge to build mathematical models as well as knowledge on composition and structure of foods, i.e., food science; it is assumed that the reader is familiar with basic principles of food science and technology.

The major part of the book is concerned with modeling the kinetics of relevant reactions in foods and deals with questions such as: what is kinetics, what are models, how do we apply kinetics to practical problems in foods, what are pitfalls and opportunities, how to deal with uncertainty, and how to interpret results. A key question to be answered is why the kinetics of reactions in foods is often different from, say, that of chemical engineering processes.

In this chapter, we discuss some important determinants of food quality. While the subject of quality deserves a book in its own right, the purpose here is to put the relationship between kinetic modeling and food quality in perspective, to be developed in subsequent chapters.

1.2 Food Quality

What then is food quality? There are many definitions and descriptions of quality. One useful but very general description is “to satisfy the expectations of the consumer.” Although the idea of quality seems to be somewhat elusive, it is important to understand the concept because, as food technologists, we need to be able to control and predict food quality attributes. Food quality attributes are all those product attributes that are relevant in determining quality. The ultimate test for quality is acceptance or rejection by the consumer. When a consumer evaluates a product, a first impression arises from so-called quality cues: attributes that can be perceived prior to consumption and that are believed to be indicative of quality. Examples are red color of meat, or information concerning the origin of the product. This leads to certain quality expectations. When the consumer starts eating, he is confronted with the physical

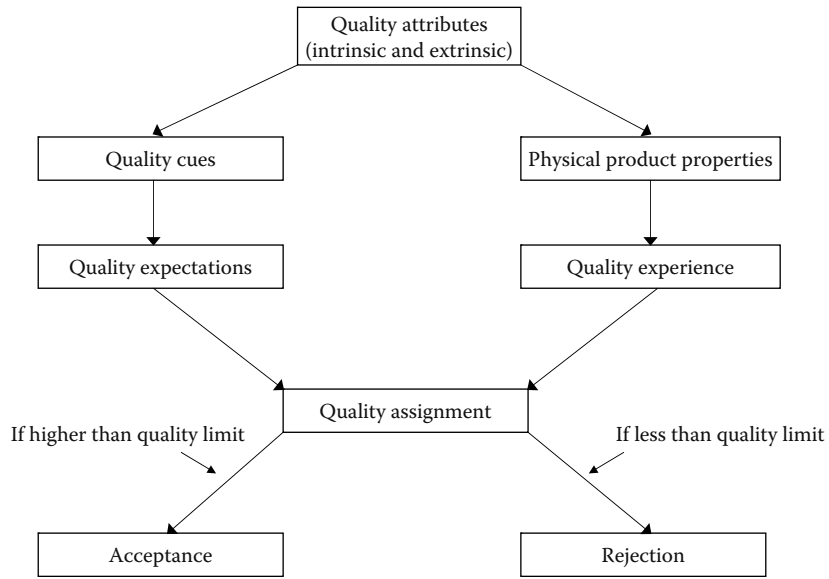


FIGURE 1.1 Schematic picture of aspects involved in quality evaluation by a consumer.

product properties (e.g., texture, taste, flavor) and this leads to a quality experience. If the quality expectation and the quality experience, integrated with each other, exceed a certain quality level, the consumer will accept the product, if not he will reject it. Figure 1.1 shows this process schematically, but the reader is advised that this scheme is an oversimplification. Quality is multidimensional, it contains both subjective and objective elements, it is situation specific and dynamic in time. A consumer however does not analyze all elements of food quality consciously but gives an integrated response based on complex judgments made in the mind.

In order to make quality more tangible for the food scientist, it is suggested to make a division into intrinsic quality attributes, i.e., inherent to the product itself, and extrinsic attributes, linked to the product but not a property of the food itself. Extrinsic factors are, for instance, whether or not a food is acceptable for cultural/religious or emotional reasons, or whether the way it is produced is acceptable (with or without fertilizer, pesticides, growth hormones, genetically modified, etc.) and its price. Extrinsic factors are therefore not part of the food itself but are definitely related to it (as experienced by the consumer). On the other hand, the chemical composition of the food, its physical structure, the biochemical changes it undergoes, the microbial and chemical condition (hazards from pathogens, microbial spoilage, presence of mycotoxins, heavy metals, pesticides, etc.), its nutritional value and shelf life, the way packaging interacts with the food, are intrinsic factors. We can propose a hypothetical quality function Q :

$$Q = f(Q_{\text{int}}, Q_{\text{ext}}) \tag{1.1}$$

In words, this equation states that quality can be decomposed in intrinsic and extrinsic quality attributes. The nature of this function remains as yet obscure. We do not know, for instance, whether we are allowed to sum intrinsic and extrinsic quality attributes, or that we need to multiply them, or do yet something else. In terms of modeling, quality assignment is usually done either from the consumer perspective or from the product perspective. It would be better if the two approaches were integrated. Techniques like quality function deployment (QFD) try to do this. We will not discuss this further in this book.

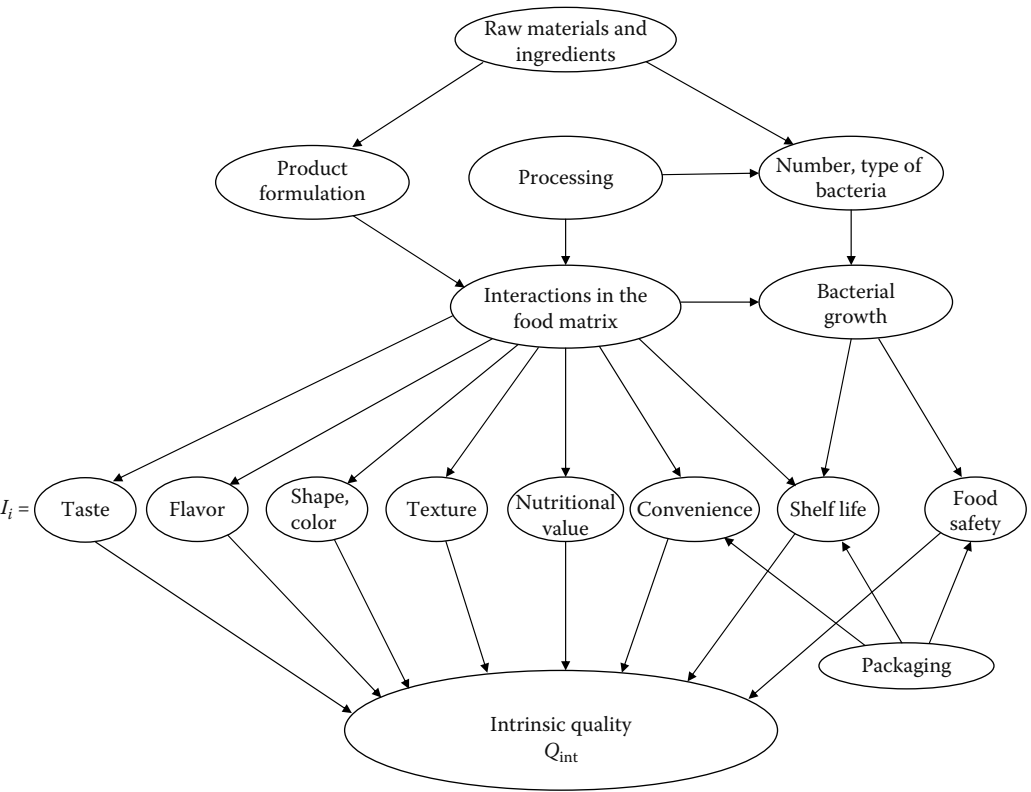


FIGURE 1.2 Schematic presentation of intrinsic quality attributes I_i .

It helps however to disentangle intrinsic and extrinsic quality attributes to make clear which factors are controllable by a technologist. Figure 1.2 shows a further decomposition of Q_{int} into intrinsic quality attributes I_i :

$$Q_{int} = f(I_1, I_2, \dots, I_n) \tag{1.2}$$

Figure 1.3 does the same for extrinsic quality attributes E_i :

$$Q_{ext} = f(E_1, E_2, \dots, E_n) \tag{1.3}$$

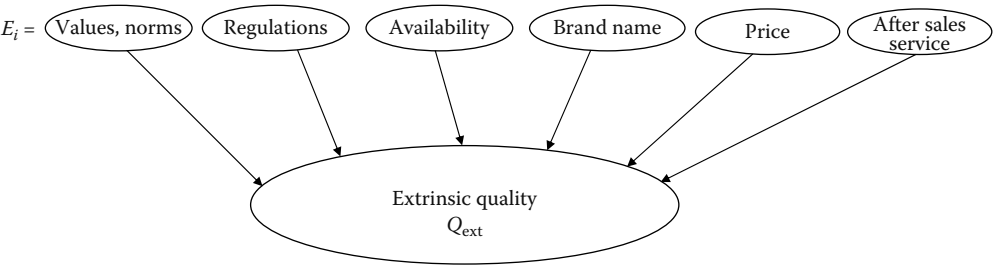


FIGURE 1.3 Schematic depiction of extrinsic quality attributes E_i .

As with the overall quality function Q , we do not know the nature of the functions Q_{int} and Q_{ext} . In other words we do not know how the quality attributes interact and are integrated by the consumer into one final quality judgment; moreover it will differ from consumer to consumer. Much more can be said about quality, but that is beyond the scope of this book. We focus now on intrinsic quality attributes. To be sure, we will not attempt to find a relation for Q_{int} in this book; rather we focus on how to characterize the listed quality attributes from a technological point of view. Even though the final quality judgment is not based on intrinsic factors alone, measurable objective quality attributes such as food safety, nutritional value, and color are of utmost importance.

In food science literature, intrinsic factors such as those mentioned in Figure 1.2 are usually called quality attributes, though this is not strictly correct as shown in Figure 1.1. To satisfy the (dynamic) expectation of consumers, with diversity in needs and markets, a producer must be prepared to be very flexible with respect to intrinsic quality attributes. Insight in these quality attributes is thus a prerequisite to survive in a competitive market. We propose that with the kinetic tools presented in this book these intrinsic quality attributes can be controlled and predicted.

Intrinsic food quality attributes can be studied at several levels as shown in Figure 1.4. With reference to Figure 1.4, this book will deal mainly with modeling activities at levels 1 and 2, with some attention to level 3 concerning the design of experiments for food product design.

Kinetic modeling of food quality attributes can be a powerful tool as part of the steps to be taken in food product development. Also, it can be the basis for the development of expert systems and management systems, especially with reference to risk analysis and food safety issues. Certain chemical reactions may serve as indicators for specific quality attributes. For instance in milk, the concentration of lactulose (an isomerization product of lactose) is an indicator of the heat treatment to which the milk has been exposed but it is not a quality attribute by itself. Clearly, the kinetics of the chemical reaction that serves as a quality indicator need to be closely related to the kinetics of the chemical or physical changes that determine the relevant quality attributes it represents. The way quality is monitored and safeguarded

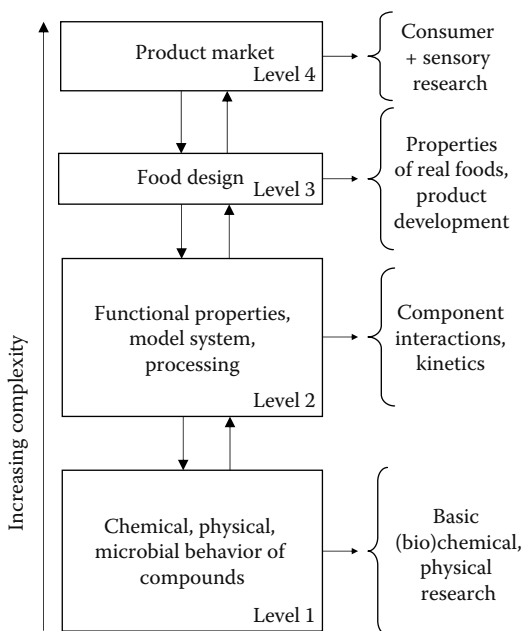


FIGURE 1.4 Several levels at which food quality can be studied.

is a particular aspect of food quality. This involves quality management, the introduction of systems such as hazard analysis and critical control points (HACCP), ISO systems, and good manufacturing practices (GMP). The statement of quality is made with reference to specific technical specifications, in other words such an approach requires integration of technological and management knowledge (techno-managerial approach). Basically, this comes down to realizing the fact that food quality is not only determined by the product itself or the technology applied but also by the people that handle the product. We will not discuss these aspects here; some references are given at the end of this chapter.

The basic message is thus that quality is not a property of the food but is determined by the consumer who translates his perception into quality attributes. Some of these attributes can be related to measurable properties of the food though this is not always possible for user-related factors. The crispness of potato crisps, for instance, relates to mechanical properties of the (fried) potato cell wall; the sweetness of pastry is related to its sugar content as well as the sweetening intensity of the sugar used; the color of a food is for the most part attributable to components that absorb light at a particular wavelength and/or scatter light. There are also intrinsic factors that cannot be perceived directly by the consumer, such as the presence of toxic components or pathogenic bacteria. Such “hidden” quality attributes can, however, in most cases be measured. This book is concerned only with intrinsic factors, and particularly how we can “capture” these quality attributes within mathematical models. The advantage of using such models is that they can be linked to other models describing for instance stimulus–response relationships and consumer preference. The following intrinsic quality attributes are the most important ones for the food scientist:

- Safety (microbial, toxic, mutagenic)
- Wholesomeness, nutritional value
- Usage (handling) properties
- Storage stability/shelf life
- Texture
- Color
- Appearance
- Flavor, taste compounds

Some of these attributes are the result of the interaction of stimuli picked up by the senses and are called sensory properties. Sensory properties can be estimated using sensory panels (though this is a different type of measurement process than using laboratory instruments). It is, however, important to make a distinction between product properties and the perception of these properties. Sensory measurements are, therefore, the result of product properties (causing stimuli) and the processing of these stimuli by the consumer.

Some quality attributes are the resultant of several phenomena. For instance, the color of a food may be the result of the presence of several components absorbing or reflecting light of a certain wavelength. Even though color can be measured instrumentally, it is not immediately obvious which compound is responsible for the color observed. Another example is the quality attribute nutritional value, which is determined not only by vitamin content but also by the type and amounts of amino acids, type and amounts of fatty acids, etc. That is why we propose to decompose quality attributes further into quality performance indicators. In the above examples, a quality performance indicator for color may be the concentration of a carotenoid, and the content of the amino acid lysine may be one of the quality indicators for nutritional value. Many quality indicators can be measured directly using physical or chemical measurements. Examples include the presence/absence of pathogenic microorganisms, the protein content and the biological value of the protein, vitamin content, bioavailability, etc. These indicators clearly cannot be determined via sensory panels; they are hidden to the consumer, although they may have a subliminal effect on food choice.

Kinetic approach. When we speak of food quality in this book we address these physical, chemical, biochemical, and microbial quality indicators. We accept that this is only a part of the quality perceived

by the consumer. However, we limit ourselves deliberately to the indicators mentioned because we consider them the principal domain of the food technologist. An important consideration is that these indicators tend to change with time, and therefore they have to be characterized by a kinetic approach, the subject of this book. Food technology is, in short, concerned with the transformation of raw materials into foods and their stabilization (preservation), taking into account all boundary conditions of food safety and quality mentioned above. Raw materials and foods are subject to change because of their thermodynamic instability: reactions take place driving the system toward thermodynamic equilibrium (as will be discussed in Chapter 3). Foods may deteriorate soon after harvesting (sometimes even during harvesting), and deterioration should be read as loss of quality. Prevention and control of this thermodynamic instability is the main task of food technologists. It is the characterization of the changes taking place that is important because this provides us with possibilities to control quality. This is then the domain of kinetics.

Kinetics plays thus an important part in the modeling of food quality. The purpose of this book is to explain how kinetics and kinetic models can be used in a meaningful way, thus to supply valuable tools to describe changes in quality performance indicators and attributes, and most importantly to supply tools to control and predict these quality indicators and attributes. Still, foods are so incredibly complex from a chemical and physical point of view that we need to resort frequently to systems mimicking foods. Otherwise, there will be so many interfering factors that the predictive capabilities of mathematical models will be very limited. Model systems mimicking foods are by their very nature simplifications but, on the other hand, they need to approach real foods in some sense. Ignoring specific properties of foods when designing model systems may lead to serious mistakes when one extrapolates from the model systems to real foods. Since this is not straightforward, a special chapter (Chapter 14) discusses this in detail for some relevant food aspects. Overall, the philosophy presented in this book is that it is essential to understand what is happening at the molecular level (occasionally the colloidal level) and for this reason the material presented is at the fundamental level of thermodynamics and chemical kinetics. It is the author's view that such understanding is needed in order to come to models that will be able to control and predict food quality. In addition, kinetic modeling as such is a tool in understanding what is going on because proposed mechanisms need to be confronted with experiments, and if the two do not match something was apparently wrong with the proposed mechanism. Having said that, it is also appreciated that we sometimes have to resort to empirical models due to the complexity of foods. This statement may seem contradictory to the philosophy that fundamental insight is needed but it is not. It is merely a recognition of the fact that our understanding of what is going on in foods is far from complete, and it would be foolish to stick to models that are derived from situations in very simple and ideal systems while they are not capable to grasp the real situation. Especially if we want to be able to predict real-life situations in a realistic way, empirical models may actually perform better than mechanistic models in some situations. That is why the reader will also be introduced to empirical models. Admittedly, empirical models will not directly provide molecular insight. It is therefore important to have attention for both approaches.

1.3 Foods as Complex Reaction Media

When considering reactions in foods, the medium in which these reactions take place is obviously of importance. We may have solid, liquid, and vapor phases in and around foods. Most of the relevant reactions in foods will take place in the liquid phase. In many cases this will be an aqueous phase but also lipid phases are possible, or ethanol may be present which gives different properties to the reaction medium. There may be partitioning between phases. Solid phases may become of importance because they may result from exceeding solubility products; an important solid phase is, of course, ice, but also salts and sugars may be present as crystalline material, or sometimes as amorphous materials. Moreover, solid phases may induce adsorption of reactants and products and catalyze or inhibit reactions. Then we have the presence of amorphous phases, like in glasses. The vapor phase is of importance when a

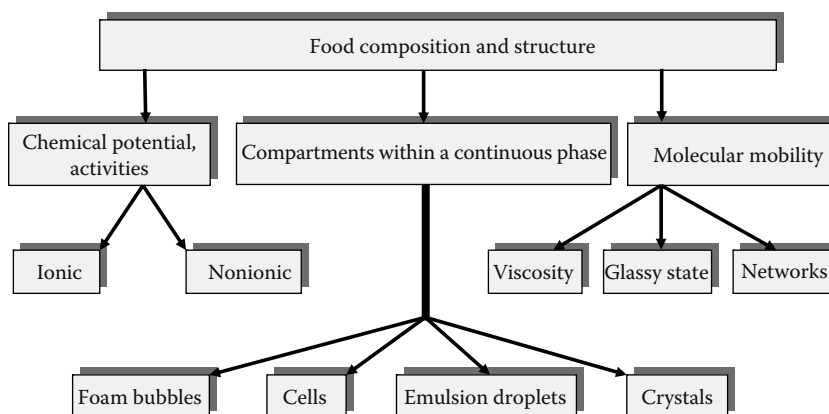


FIGURE 1.5 Overview of the complexity of foods as reaction media.

headspace is present, or in the case of foams, and the partitioning of volatiles is a very relevant phenomenon in relation to sensorial aspects. When we want to study kinetics in foods, we have to take all these various aspects into account, but there are few, if any, theoretical frameworks available with which to do this. Most theories have been developed for ideal, dilute, and homogeneous systems. Foods are multicomponent, concentrated systems with various phases present at the same time, and consequently foods behave all but ideal. Complications with foods arise because of deviations from simple diffusion laws, complications with molecular mobility, partitioning phenomena, and volume exclusion effects. These questions will be addressed in the book. The food matrix is usually very complex, consisting of water-insoluble material (e.g., cell membranes), a complicated aqueous solution of ionic and nonionic compounds of high and low molar mass, amorphous materials, various phases (fat globules, foam bubbles, crystals), and to complicate matters further, foods can also be in a glassy state. All this has a large impact on kinetics. Figure 1.5 summarizes the aspects involved, and serves as a guideline for the topics to be discussed in this book.

1.4 Outline of the Book

After this introduction, the book is divided in two parts. The first part is called “The basics” and attempts to describe the first principles of modeling (Chapter 2), thermodynamics (Chapter 3), chemical kinetics (Chapter 4), temperature and pressure effects (Chapter 5), and charge effects (Chapter 6). Chapter 7 introduces the use of statistics in kinetics. In the author’s view this is a crucial topic that deserves a great deal of attention and the topic is therefore treated at some length. Though the treatment in Part I is basic and general, food examples are used wherever possible. Part II is called “Application of the basics to chemical, biochemical, physical, and microbial changes in the food matrix,” in which we direct our attention subsequently to chemical, physical, biochemical, and microbiological aspects relevant for foods. Thus, Chapter 8 discusses the possibilities and advantages of multiresponse modeling, a topic that lends itself very well for food science problems, especially when they are of a chemical nature. Surprisingly, the concept is hardly used in food science literature, and accordingly we describe the principles, applications, and potential problems in detail and apply it to some chemical changes. As indicated above, there is more to food quality than chemical changes. The chapters to follow are devoted to enzyme kinetics and kinetics of protein and enzyme inactivation (Chapters 9 and 10), kinetics of physical processes (Chapter 11), kinetics of microbial growth as well as inactivation (Chapters 12 and 13, respectively). Chapter 14 attempts to address specific problems arising in the food matrix when dealing with kinetics. This concerns discussions as to why kinetics in foods can be quite different from reactions in simple model

systems in test tubes, how we can identify such problems and take them into account when using model systems (to get around the problem of variability and complexity). Finally, we give a retrospective and an outlook by discussing some trends and developments in modeling in general and with some attention for shelf life modeling in particular because that requires integration of several aspects (Chapter 15).

Bibliography and Suggested Further Reading

About Quality

- Aguilera J.M. and Lilford P. *Food Materials Science. Principles and Practice*. New York: Springer, 2008.
- Bruin S. and Jongen T.R.G. Food process engineering: The last 25 years and challenges ahead. *Compr Rev Food Sci Food Saf* 2:42–81, 2003.
- Damodaran S., Parkin K.L., and Fennema O.R. *Fennema's Food Chemistry*. 4th ed. *Food Science and Technology*, p. 1144. Boca Raton: CRC Taylor & Francis, 2008.
- Jongen W.M.F. and Meulenbergh M.T.G. *Innovation in Agri-Food Systems. Product Quality and Consumer Acceptance*, p. 399. Wageningen: Wageningen Academic Publishers, 2005.
- Fito P., LeMaguer M., Betoret N., and Fito P.J. Advanced food process engineering to model real foods and processes: The “SAFES” methodology. *J Food Eng* 83:173–185, 2007.
- Gaonkar A.G. and McPherson A. *Ingredient Interactions. Effects on Food Quality*. 2nd ed., p. 554. Boca Raton: CRC Taylor & Francis, 2006.
- Kind M. Product engineering. *Chem Eng Process* 38:405–410, 1999.
- Labuza T.P. and Riboh D. Theory and application of Arrhenius kinetics to the prediction of nutrient losses in foods. *Food Technol* 36:66–74, 1982.
- Labuza T.P. Application of chemical kinetics to deterioration of foods. *J Chem Educ* 61:348–358, 1984.
- Linnemann A.R. and Van Boekel M.A.J.S. *Food Product Design. An Integrated Approach*, p. 236. Wageningen: Wageningen Academic Publishers, 2007.
- Lund D. Predicting the impact of food processing on food constituents. *J Food Eng* 56:113–117, 2003.
- Luning P.E., Marcelis W., and Jongen W.M.F. *Food Quality Management*. Wageningen, the Netherlands: Wageningen Pers, 2002.
- Luning P., Devlieghere F., and Verhé R. *Safety in the Agri-Food Chain*, p. 688. Wageningen: Wageningen Academic Publishers, 2006.
- Martens H. and Martens M. *Multivariate Analysis of Quality*. Chichester: John Wiley & Sons, 2001.
- Molnar P.J. A model for overall description of food quality. *Food Qual Pref* 6:185–190, 1995.
- Niranjan K. Chemical engineering principles and food processing. *Trends Food Sci Technol* 5:20–23, 1994.
- Norton I., Fryer P., and Moore S. Product/process integration in food manufacture: Engineering sustained health. *AIChE J* 52:1632–1640, 2006.
- Saguy I. and Karel M. Modeling of quality deterioration during food processing and storage. *Food Technol* 34:78–85, 1980.
- Sloof M., Tijskens L.M.M., and Wilkinson E.C. Concepts for modelling the quality of perishable products. *Trends Food Sci Technol* 7:165–171, 1996.
- Tijskens, L.M.M. *Discovering the Future: Modelling Quality Matters*. PhD thesis, Wageningen University, the Netherlands, 2004.
- Van Boekel M.A.J.S. Kinetic modeling of food quality. *Compr Rev Food Sci Food Saf* 7:144–157, 2008.
- Van Trijp H.C.M. and Steenkamp J.B.E.M. In: *Innovations in Food Production Systems*. Jongen W.M.F. and Meulenbergh M.T.G. (Eds.). Wageningen: Wageningen Press, 1998.

I

The Basics

2

Models and Modeling

2.1 Introduction

Since this book is about kinetic modeling, it is appropriate to explain the philosophy about models. Models are certainly not a panacea for all problems. They offer opportunities but also have limitations. It is essential that the reader be aware of this and it is the intention of this chapter to provide this basic awareness.

2.2 Models and Modeling

So, what are models and what is modeling? The answer is not straightforward because it depends on the goals of modeling and the type of model used. Generally speaking, models attempt to formulate the behavior of systems from knowledge of the properties of their component parts. Invariably, models are simplifications of the real world, designed to facilitate predictions and calculations. They are a tool to help us handle complex situations. Thus, the modeler should be under no illusion with regard to the physical reality of models. Models exist in the mind of the scientist, not in nature. Modeling is an attempt to approximate the real world (the truth), but the truth (whatever that is) will never be reached (if we would know the truth it would not be necessary to use models). This does not detract at all from the usefulness of models but an awareness of the nature of models will help us to see the opportunities as well as the limitations. Thus, models can be seen as a way of communicating a view of the world and they are open to scientific debate. This applies, of course, equally well to kinetic modeling of reactions in foods.

Let us try to picture the various ways in which we can use models to describe a system. Suppose that an input is given to a system that will respond with an output: see Figure 2.1. If we know the input I and we can measure the response R , we can use a model to learn about the system S . For instance, if we heat a food (heat is the input) and we measure the effect on protein denaturation (the response) we could learn something about the behavior of proteins in that particular food matrix (the system). If we know the input I as well as the system S , we can use a model to predict the response. For instance, if we know how much heat we put into a system and we know how the proteins in the system respond to this, we can predict the level of denaturation. If we know the system S as well as the response R it produces upon a certain input we can use a model to control, or to design, which input we need to produce a desired output. For instance, if we want to achieve a certain level of protein denaturation in a food, then we can calculate how much heat is needed to achieve this. These simple examples show that models can be used for various goals. In relation to food quality, all three goals are important. Our system is the food, inputs can be processing conditions, and responses can be changes in food quality attributes. We can use models to learn about the “physical” processes taking place in the food that govern food quality attributes, to

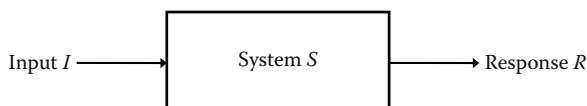


FIGURE 2.1 System S responding to an input I by a response R .

predict food quality attributes as a function of inputs for a given food, and to control food quality for a given food by managing the input. It is perhaps meaningful to spend a few more words on the concept of prediction because there seems to be some confusion on this in literature. A distinction should be made between “model fit” and “prediction.” A model fit is obtained when comparing the performance of a model with the experimental data. Prediction means that it is possible, via models, to predict events or situations that were not in any way used in setting up the model. This can be future events, or events that were obtained independently in other studies. To be clear, we use the words model fit and prediction in this sense throughout the book.

Schemes such as in Figure 2.1 are sometimes referred to as conceptual models, i.e., a hypothesis about how a system works and responds to changes in inputs. In other words, it is a set of qualitative assumptions. If we are able to turn somehow these qualitative assumptions into quantitative ones, and if we can describe this with mathematical equations, a conceptual model changes into a mathematical one. Throughout this book, we will confine ourselves to models that describe “physical” phenomena in a mathematical way, i.e., chemical, physical, or microbial events are translated into mathematical equations. Examples include the nonenzymatic browning of foods, the growth of bacteria in a food, and the sedimentation of cocoa particles in a chocolate drink.

Mathematical models relate responses to variables via parameters in one or more equations. Say that we are interested in the fate of a vitamin in a food during processing and storage, as a measure for a change in nutritional quality. What is useful to know then is the change in concentration of such a vitamin over time at a certain temperature, or possibly at fluctuating temperature. As we will see in later chapters, a possible mathematical relation that describes the vitamin concentration (denoted as [vitamin]) as a response to the variables time t and temperature T could be:

$$[\text{vitamin}] = [\text{vitamin}]_0 - A \exp \left[-\frac{E_a}{RT} \right] \cdot t \quad (2.1)$$

$[\text{vitamin}]_0$ represents the initial concentration. A and E_a represent parameters characteristic for the degradation of the vitamin in the food under study (these are the pre-exponential factor A and the activation energy E_a in the Arrhenius equation, Chapter 5). Such parameters can be estimated in controlled experiments. The parameter R is a fundamental physical constant (the gas constant), which is known and need not be estimated. Preferably, the parameters should be physically interpretable. Time and temperature are controllable variables that can be manipulated by the experimenter or operator. If an equation such as Equation 2.1 is established and the parameters estimated from experimental results, one could then, in principle at least, control and predict the change in vitamin concentration at any relevant time and temperature because we can control time and temperature, and thereby control this food quality indicator.

Quality change modeling. We can generalize this further by following the food along its way in the food production chain. Generally, there will be changes in food quality when the food moves from the producer to the consumer; quality is not static. There may be losses, for instance of vitamins during storage of fruits and vegetables. On the other hand, the nutritional value of a processed food may increase as compared to the raw material, for instance, bioavailability or digestibility may be enhanced. To illustrate this change in quality, suppose that a quality performance indicator (for instance the concentration of a vitamin) is built up during the growth of a vegetable or a fruit. Loss of quality usually starts immediately after harvesting, so postharvest storage may already result in some losses. Processing may perhaps result in

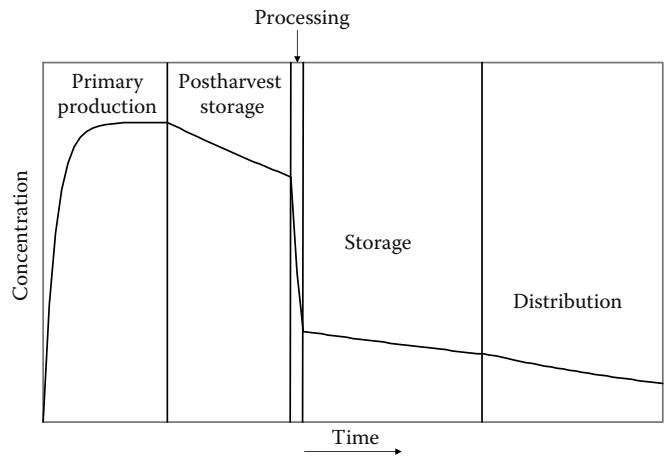


FIGURE 2.2 Schematic depiction of change in a quality performance indicator (e.g., vitamin concentration) along the food processing chain.

much higher losses, while storage and distribution may give a further gradual decrease of quality. Figure 2.2 gives a schematic example of such a quality loss. For modeling purposes, it is convenient to identify and quantify the various factors leading to quality changes in each chain element. The output of one chain element is the input for the next (Figure 2.3); a production chain can be seen in this way as a cascade of unit operations. We propose to describe this as quality change modeling. In doing so, various models need to be connected to each other with proper use of mass and energy balances. However, if we want to maintain a high quality at the end of the chain, i.e., when the food arrives at the consumer, the trick is to optimize quality all over the chain, rather than locally in one of the chain elements.

By analyzing quality in this way, it becomes possible to optimize quality from an analysis of what happens in the various elements in the food chain. Analogous to the term HACCP, we propose to describe this as Quality Analysis Critical Control Points (QACCP). In the case of a situation as in

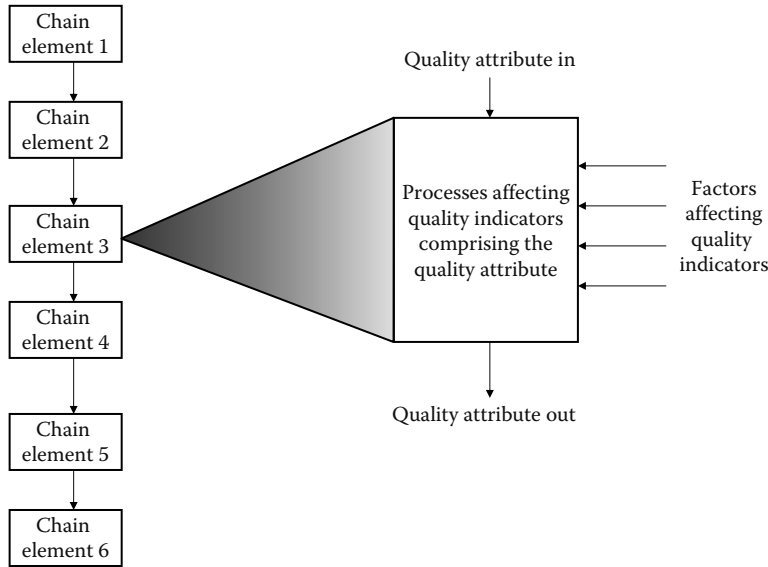


FIGURE 2.3 Schematic presentation of quality models in elements of the food chain.

Figure 2.2, it is clear that much could be improved in the processing step, so that attempts to increase quality should focus on processing conditions. In other cases, losses during storage or distribution may actually be larger than in processing, and then storage conditions may have to be optimized (for instance, by changing temperature, or relative humidity). In order to be able to derive graphs such as Figure 2.2, one must understand what is happening to that particular quality attribute. The main theme of this book is to apply methods correctly to describe such changes quantitatively in every element of the food chain. Mass and energy balances may be helpful in this respect because terms in such balance equations involve kinetics. To be sure, changes in quality attributes as depicted in Figure 2.3 apply, of course, also to microbial growth as a (negative) quality factor, which is the subject of much research nowadays, sometimes referred to as predictive microbiology, or quantitative microbiology. Of course, much work has already been done and published in the past. Unfortunately, many of these studies published cannot be used to develop predictive models because external conditions as well as essential information on the food were not reported. It is also essential that quantitative data are reported in full rather than as averages for developing and validating models.

Deterministic empirical and mechanistic models. If we now generalize equations such as Equation 2.1 in a more abstract way, a description of a mathematical model can be given as:

$$\eta = f(\theta, \xi_v) \quad (2.2)$$

where

η represents measurable response(s) (such as vitamin concentration in Equation 2.1)

θ symbolizes the parameters of the model (A and E_a in Equation 2.1)

ξ_v represents the controllable variables (t and T in Equation 2.1)

The notation $f(\dots)$ should be read as: “is a function of.”* In kinetic models, η would thus represent concentrations or rates; θ rate constants, activation energies, diffusion constants; and ξ_v reaction time, temperature, pressure, or initial concentrations. The main purpose of kinetic modeling is to cast the relevant quality attribute in some mathematical equation and to find the actual form of Equation 2.2, followed by estimation of the characteristic parameters.

There may be two different objectives for setting up a mathematical model in the form of Equation 2.2:

1. To obtain an estimate of responses over a range of variables that are of interest, either by interpolation between experimental measurements or in a predictive way.
2. To determine the underlying physical mechanism of the process under study, i.e., to find the nature and significance of the function $\eta = f(\theta, \xi_v)$.

For objective 1, a theoretical model is not really needed, although it could be useful if one is to stray outside the boundaries of experimental measurements. All one needs is a suitable mathematical function (such as a polynomial function) that accurately describes the experimental results. This is often referred to as empirical modeling or response surface methodology (RSM). It can be very useful for situations where an underlying mechanism is not readily available. The approach obviously has its limitations. It cannot be used to build a mechanistic model because the parameters have no physical significance. It is also very dangerous to extrapolate outside the region of variables for which the function was derived (and sometimes even interpolation is tricky).

The situation is different for objective 2. Here a scientific theory is required on which to base a mathematical function. While a model can never represent the complete real world, an adequate mechanistic model should be based nevertheless on a scientific theory and the model should be able to predict experimental results or commonly observed phenomena accurately. The parameters in the model

* The notation in Equation 2.2 using Greek symbols is commonly used in the statistical literature. We adopt this here because we will apply statistics frequently in this book.

should have physical significance and in the field of kinetics they include, for instance, rate constants and diffusion coefficients. It is also of importance to state the conditions clearly under which the parameters have been defined. It should be less dangerous in this case to extrapolate outside the experimentally tested regions.

The two types of models, empirical and mechanistic, represent extremes; in reality the situation is somewhere in between, certainly for foods with all their complexity. Thus, even with empirical models, one may have some idea of the underlying mechanism. For instance, some microbiological growth models are, strictly speaking, empirical because the manner in which water activity or pH affect microbial growth is not (fully) understood. On the other hand, the functional behavior of the response, e.g., whether linear or logarithmic with respect to pH, may provide clues as to the underlying mechanism. Conversely, a model that is claimed to be mechanistic may still contain unexplained aspects; a rate constant, for instance, can be apparent, i.e., reflect more than one reaction step, as discussed in Chapter 4.

Stochastic models. At this point it is essential to introduce yet another element in the discussion about models. Mathematical models as such are deterministic, i.e., they produce a certain outcome, usually expressed in a number (e.g., a vitamin concentration). The model displayed in Equation 2.1 produces a so-called point estimate (when the parameters are known and the controllable variables time and temperature are set). However, we do not live in a deterministic but rather in a stochastic world (from the Greek word “στοχαστικός,” meaning guessing, surmising) and a number as such can be misleading because it suggests certainty. In other words, deterministic models provide an answer that is in a sense not realistic because it ignores (random) variability. When we use models to predict something, we have to accept that there will be an element of uncertainty in our prediction. Suppose, for instance, that we are able to predict the content of a vitamin as predicted by Equation 2.1 as a function of time and temperature. We want to use this to predict the shelf life of a product; when the concentration falls below a certain level the product is not deemed acceptable anymore. This could result in a graph as depicted in Figure 2.4A: A critical time t_c can be estimated from this. At a time longer than t_c the product is not acceptable anymore. However, because there is uncertainty in the value of the parameters A and E_a , there will be uncertainty in the outcome as well and this results in variation in the prediction and consequently the estimation of critical times t_c is also variable (Figure 2.4B). If we are somehow able to estimate this variation, it will be possible to predict the uncertainty, and this will usually be in the form of a probability distribution, in this case of critical times t_c (Figure 2.4C). Incidentally, this probability distribution need not be a normal distribution.

Variability and uncertainty. Uncertainty, in other words, can and should be modeled! In this respect, it is useful to subdivide the total uncertainty in its two constituents *variability* and *uncertainty*. Variability comprises the natural variation in the real world. For foods, this comes down to the biological variation in the composition of raw materials and in the behavior of living materials, especially microorganisms. It can also relate to such things as a slightly varying temperature in a supply chain: even though the temperature may be fixed at a certain value, it will show some stochastic variation that will have an effect on the outcome of our prediction. This variation is inherent in the nature of our physical world. We can measure this variation via statistical methods, but we cannot reduce it (at least not without changing the system). Incidentally, this is often the very purpose of using controlled model systems that simulate behavior of foods, for instance by using a solution of an amino acid and a reducing sugar to simulate the Maillard reaction occurring in foods. In this way we can control or even eliminate biological variation and direct our attention to the reaction of interest, which is very useful to understand the mechanism at hand, but when we translate the results back to real foods we should not forget the biological variation. In fact, variability does give important and essential information about the system under study and should be studied accordingly.

The other element is uncertainty. This reflects the state of our knowledge (or ignorance) about the system. For instance, a parameter (such as an activation energy) in a mathematical model can be estimated from data but there will be an error involved in this estimate because the data are obtained by using an error-prone method. By doing more experiments (and perhaps better designed when we get

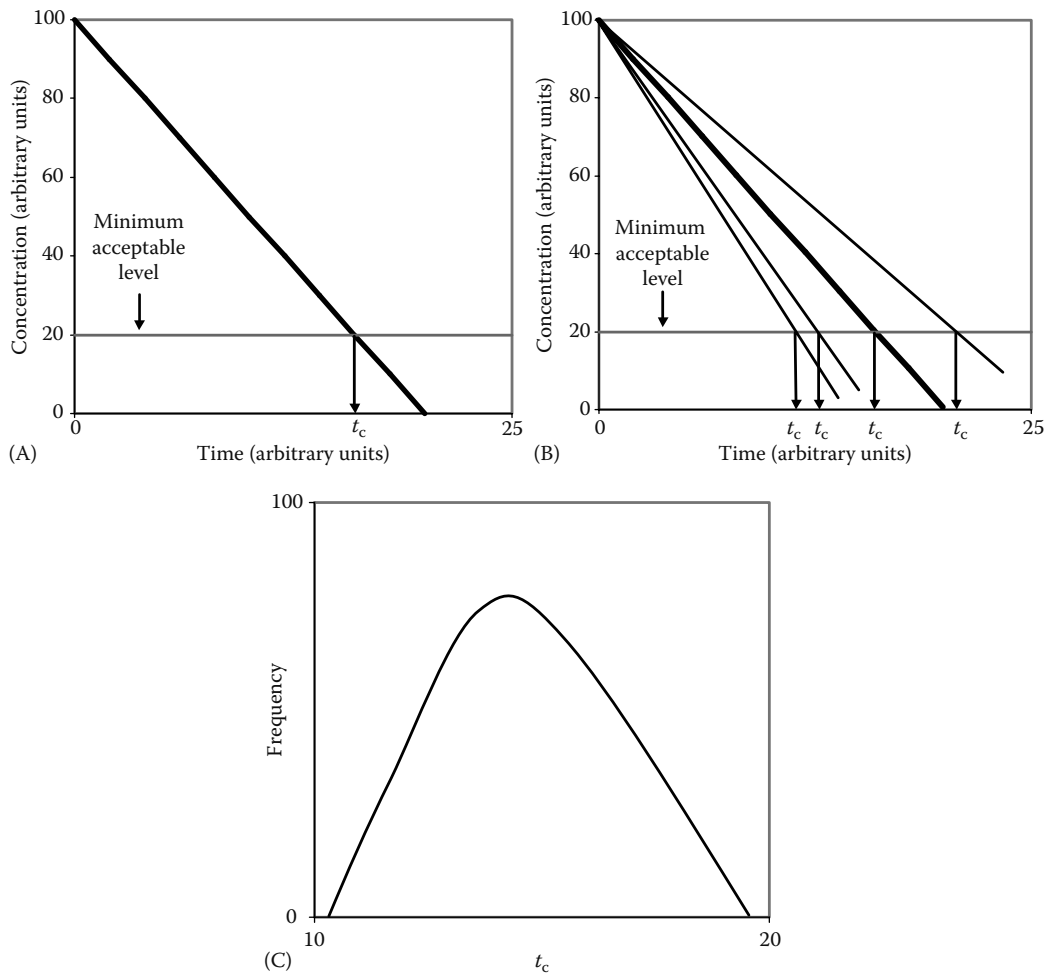


FIGURE 2.4 Hypothetical example showing the prediction of the change in vitamin content as a function of time at constant temperature. t_c is the time at which the minimum acceptable level is reached. Deterministic result (A), variable result because of uncertainty in the parameters (B), frequency distribution for the critical times t_c (C).

to know the system better) we can reduce this uncertainty. This is the very reason why it is useful to split total uncertainty up into variation and uncertainty. If total uncertainty is determined mainly by variation, it makes no sense to try to reduce the uncertainty by doing more measurements. If it is, however, determined by uncertainty we can reduce total uncertainty by doing more and better measurements. Such considerations are very important for risk–benefit analyses in a broad sense, i.e., not only microbial risk assessment but also optimization of concentration or bioavailability of certain food components (benefit assessment). A very good impression of total uncertainty can nowadays be obtained via Monte Carlo simulation (for which we need probability models, to be discussed later). It is the author’s opinion that this way of thinking will become increasingly important for food design problems. It means that we should be prepared to introduce elements of stochastic modeling into our mathematical models, i.e., to introduce probability distributions rather than point estimates in our model. So, instead of a fixed value for the activation energy in Equation 2.1 we could insert the probability distribution of the activation energy in the equation (reflecting our state of ignorance) and simulate stochastic variation in the prediction by drawing random numbers by computer. This is done typically thousands of times

(i.e., Monte Carlo simulation) and results in a probability distribution of the outcome, i.e., a description of the range of values that the outcome may take together with the probability that the variable will take any specific value. A probability can be seen as a numerical measurement of the likelihood of an outcome. This stochastic nature of modeling is the reason why we spend considerable attention to statistics in this book. Not every scientist seems convinced of the usefulness of statistics, sometimes expressed in the phrase “how to lie with statistics.” This is unfortunate because statistics should be seen as an important tool in the scientific learning process, to cope with the phenomena of variability and uncertainty, and to be able to draw general conclusions from a limited amount of data. A very useful branch of statistics is the so-called Bayesian statistics, especially in relation to modeling. Bayesian statistics treats probability as plausibility of a hypothesis in view of data obtained and expresses this as a so-called posterior probability, whereas “classical” statistics interprets probability in terms of frequency (a proportion in a large number of repetitions of the random process), and uses significance tests to see if a hypothesis can be confirmed. There are fundamental differences in the two approaches and few food technologists appreciate Bayesian statistics, as they have been trained, most likely, in classical statistics. We consider Bayesian statistics important enough to introduce it and discuss some of its elements in Chapter 7. It is also important for risk-benefit analysis and decision analysis concerning food safety.

Model uncertainty. We now come to a very important philosophical point in modeling. What we actually are trying to do is to approximate truth or reality with our models. However, it is important to realize that we will never be able to capture reality fully (if we could we would not need a model). The only thing we can do is to infer something from the data that we have obtained (either by observational studies or by doing planned experiments, but we will not consider observational studies in this book). So, in other words, we try to capture the truth behind the data, i.e., the processes or mechanisms that cause the data to be as they are; we do not model the data themselves. It is the information contained within the data in which we are interested and that is expressed in mathematical models. How do we know that we select models that come as close to the truth as possible? Information theory is quite helpful in this respect, providing tools to aid in model selection. We will discuss this in some detail in Chapter 7. For the moment it is important to realize that more than one model may come close to the truth (even though we will never know what truth is). We stress this point because this is the essence of modeling: we will never reach truth (and we do not need to!) as models are just approximations. The important consequence is however that this aspect adds to uncertainty, namely the uncertainty as to how far the model is away from the truth. Figure 2.5 gives some hypothetical situations.

With reference to Figure 2.5 it is obvious that model 1 comes reasonably close to reality, model 2 follows the trend to some extent but with considerable bias, and model 3 is completely off. Obviously, we

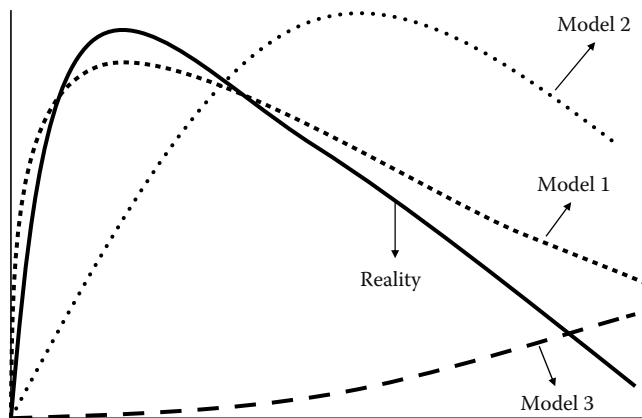


FIGURE 2.5 Hypothetical examples of “reality” and three models that approximate reality.

would like to reduce this model uncertainty but, because we do not know the truth we cannot measure this in an absolute sense, only in a relative sense. One such measure is the so-called Akaike criterion, discussed in Chapter 7. The Akaike criterion focuses on predictive accuracy and provides a methodology to see which model performs the best in predictive accuracy. The topic of model discrimination, i.e., differentiation between a good model and one that is less good, or a bad model, is thus another essential topic. A good model is able to extract the relevant structural information from the data and separate this essential information from noise. It may be that more than one model applies, and the choice for a particular model introduces again uncertainty in our endeavor to approximate to the truth. In some cases it may be better to do some form of model averaging rather than choosing just one model. Some methods of model discrimination are discussed in Chapter 7. By comparing models we actually evaluate the amount of information in the data relative to the information capacity of the model (the more complex the model, the more information capacity it has).

So, it should be clear by now that models are always wrong, but some of them may be useful (to paraphrase the famous statistician George Box). Box and coworkers (see bibliography at the end of the chapter) suggest that one should “tentatively entertain a model” rather than assume it to be correct. This implies that one should always be prepared to put models in jeopardy, and subsequently revise them in the light of new evidence. This is the very basis of the scientific method, where hypotheses and theories are subject to peer review and amended (or indeed rejected). The process of modeling is, therefore, iterative in nature (Figure 2.6).

All the elements in this iterative cycle are essential for modeling. Although a cycle is depicted in Figure 2.6 with no apparent starting point, we suggest that, whenever possible, the cycle is started with the box called conjecture. The reason for this is that this is the point where science comes in (for food science basically (bio)chemistry, physics, and microbiology). In the case of a chemical reaction, for instance the Maillard reaction, it helps enormously if the researcher is aware of the possible basic mechanisms because that will give structure to the planning of subsequent experiments. It also means that the researcher should propose some possible models already at this stage, which will be tested and compared later on. This conjecture can be a very simple idea based on literature, observation of the phenomena, basic chemical knowledge, or even intuition. In any case, it is important to think hard before doing experiments and to ask the right questions and apply the appropriate science. Admittedly, there may be situations in which it is impossible to pose models beforehand, and that one needs to do some starting experiments in order to get a feel for the problem at hand. However, in most cases, there will be some idea of an approximating model. Experiments are designed to test the original idea.

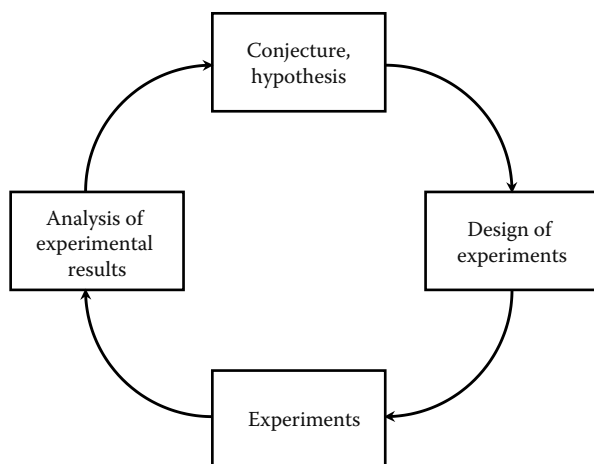


FIGURE 2.6 Scheme showing the iterative nature of the various stages in modeling.

Experimental design is an essential part of modeling, and its importance is often overlooked. Statistical methods are available to support this stage of experimental design. The design determines and limits the information that can be obtained from a data set. The goal of experimental design is to optimize the information content of a data set with the least possible effort. Experimental design is likely to depend on the purpose of the investigation, whether it be model discrimination or parameter estimation. Chapter 7 pays attention to this aspect of kinetic modeling. Doing the actual experiment can be relatively straightforward in principle, but may be complicated in practice. For instance, with an experiment designed at one temperature the heating-up time may be considerable and cannot be neglected.

For the analysis of the data, the use of statistics is indispensable because experiments always contain noise (i.e., noninformation caused by unexplainable variation) and we need to be able to differentiate between this noise and essential information contained in the data. Once again we stress that we are trying to model the information contained within the data, not the data themselves. With properly analyzed results, the original idea can be tested for its validity (or if more than one model had been proposed, model discrimination is accomplished). This may well lead to adjustment of the original idea (the objective is not to accept or to reject a model but to improve it). Experimental data only become meaningful in the framework of a model, as data in isolation do not provide this type of information. However, a model is never definitive and we must accept the iterative nature of modeling. The already mentioned Bayesian statistical approach fits very well into this philosophy because it describes this learning process in a mathematical way: prior knowledge and data are combined in posterior knowledge, as discussed in Chapter 7. In any case, the combined use of statistics and mechanistic understanding is needed here because it will be necessary to differentiate between noise in the data and the information contained within the data.

Model parameters. Model parameters constitute the core of a model. One should always strive for the lowest number of parameters possible in a given model because, as it happens, any model will fit a data set if the number of parameters is made high enough. The penalty for this so-called overparameterization is that the model will be indiscriminate and often worthless: the variance of the parameters will increase too much for proper use of the model (e.g., making predictions). Fortunately, proper use of statistics could signal this and appropriate measures can be taken, as discussed in Chapter 7. On the other hand, if the number of parameters is lowered, the bias between the model and the data increases. Modeling is thus a delicate balance between over- and underparameterization. Figure 2.7 illustrates this. It is in fact a depiction of a famous quote from Einstein: “Models should be as simple as possible but no simpler than

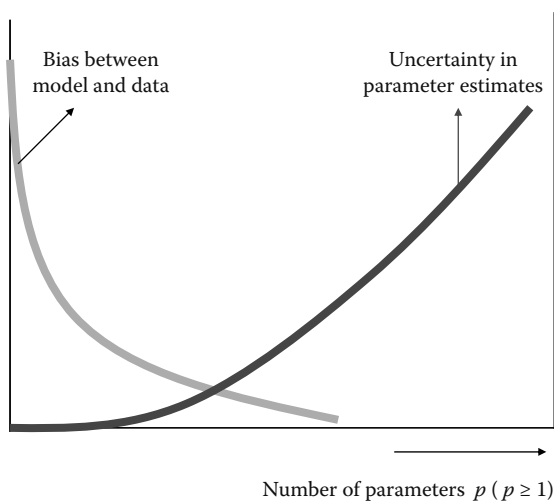


FIGURE 2.7 Schematic picture showing the bias between a model and experimental data and the uncertainty in parameter estimates as a function of the number of parameters in a model.

that.” *As simple as possible* refers to the idea that models should simplify reality taking into account the details that matter and neglecting the details that are not so important. *No simpler than that* means it should be possible to do calculations with the model that tell the essential things about reality.

An interesting situation may arise when mechanistic insight requires a certain parameter, whereas the statistical analysis tells us that that parameter is redundant. It may be that the data set does not contain enough information to estimate the parameter, or it may be that the mechanistic insight needs revision. In any case, a sensible interplay between statistics and mechanistic knowledge (chemical, physical, microbiological, and biochemical in the case of foods) is required. The following guidelines are of importance, and are discussed in more detail in following chapters.

1. The art of keeping the number of parameters in a model at a minimum is called the principle of parsimony, or Ockham’s Razor (after the fourteenth century English philosopher William of Ockham) stating that “things should not be multiplied beyond necessity,” or “shave away all things unnecessary.”* In other words, a simple model is better than a complex one, but as indicated above a right balance needs to be found between over- and underfitting. A proper procedure for model discrimination will contain a penalty function for increase in the number of parameters. This is discussed in Chapter 7. Also of importance in this respect is that the greater the number of parameters, the greater the extent of nonlinear behavior (in the case of nonlinear models), also discussed further in Chapter 7.
2. *Parameterization.* The extent to which parameters in nonlinear models behave nonlinearly varies greatly. It may be that some parameters need to be reparameterized in order to find the best estimation properties. This is discussed further in Chapter 7.
3. *Range of applicability.* The data should cover the full range over which the model is applied. This is further explained in subsequent chapters.
4. *Stochastic specification.* It is very important to model not only the underlying mechanism but also the error terms involved (i.e., uncertainty). This is discussed extensively in Chapter 7.
5. *Interpretability.* Preferably, the parameters should have a physical meaning and not just be fit parameters. This is in fact one of the main themes of the book. In relation to kinetics it is discussed in depth in the following chapters. A complicating factor may be that a conflict arises between interpretability of parameters and their statistical estimation properties.

To summarize, the aims of modeling in the food science area are as follows:

1. Models can be very helpful to control and predict food quality and provide a tool to optimize quality and costs.
2. Critical points determining quality along the various elements of the food production chain can be identified.
3. Research results in different domains of the food chain can be combined.
4. Models provide tools to identify biological variability as well as uncertainty of parameters and thus provide a basis for structured data acquisition.

It is very helpful to state a goal as well as a purpose when building a model, e.g., to develop a microbial growth model (the goal) to predict microbial shelf life (the purpose). The goal can be different for different purposes. It is quite common to make several assumptions when applying models, for instance, that a constant pH exists, etc. It is necessary to state these assumptions explicitly and to consider them again after a model is used: were the assumptions reasonable for the problem at hand, or are perhaps one or more of the assumptions violated? This may help greatly in evaluating the usefulness of a model.

* The relevant statements that can be found in William of Ockham’s writings are “Pluralitas non est ponenda sine necessitate” (one should not pose more things than is necessary) and “Frustra fit per plura quod potest fieri per pauciora” (it is vain to do with more what can be done with less). The statement “Entia non sunt multiplicanda praeter necessitatem” (entities should not be multiplied unnecessarily) was probably made by a later scholar. See: www.weburbia.com/physics/occam.html

Modeling and mathematical terminology. Mathematics should be seen as a language to express relations in a concise, logical, and straightforward way. It may be helpful for the remainder of the book to explain briefly some commonly used terms. Mathematical models in relation to kinetics can appear in several forms. When systems are not changing in time, the state of that system remains constant (static). Variables describing the state of the system (e.g., temperature, concentration) do not change in time in such cases. Models describing such a condition are named *static models* or *steady-state models*. Incidentally, steady state is not synonymous with equilibrium, and equilibrium is a special case of a steady-state situation. Equilibrium is a thermodynamic concept. A system is in equilibrium when its free energy cannot be decreased any further under the conditions applied (Chapter 3). A mass balance is typically a static model. A chemical reaction in equilibrium is described also by a static model. Static models can be described with algebraic equations. When a model describes a system that changes in the course of time, as will be the case with most (if not all) reactions in foods, we speak of a *dynamic model*. Dynamic models are typically described by ordinary differential equations (ODEs), relating the state of a system (such as a concentration) to the rate of change of that state (change in concentration). Another classification is that of spatial models, when things are not only changing in time but also as a function of space. These can be described by partial differential equations (PDEs).

It is important to realize that much information can be obtained from systems that are changing. A system in steady state that is disturbed at a certain moment will respond to this disturbance and find its

TABLE 2.1 Overview of Terminology Used with Mathematical Models

Term	Description
Mechanistic model	Mathematical model based on a mechanism; a translation of a physical, chemical, and biological theory
Empirical model	Mathematical model that is optimized to give the best fit to the observed data without an underlying chemical, physical, or biological theory
Deterministic model	Gives outcomes as exact numerical values (point estimates); it produces always the same output with the same input
Probabilistic model, stochastic model	Gives an outcome with associated total uncertainty (as a probability distribution); it does not produce exactly the same output with the same input
Static/steady state/stationary model	A solution of the state equations when the time derivatives of the state variables are all set to zero, i.e., described by algebraic equations. No description of future states
Dynamic model	Results depend on time and space, described by differential equations. Representation of future system states or conditions
Linear model	A model that is linear in the parameters (not necessarily a linear relationship between x and y)
Nonlinear model	A model that is nonlinear in the parameters
Spatial models	Objects have a position in space (or a finite region in space)
State variable	Quantity describing the state of the system (e.g., concentration at a certain time)
Independent variable	Variable that determines the change in the state of the system (usually time and space) and is controlled by the modeler/experimenter
State equations	Equations that specify the particular solution (initial values, for instance) for state variables as a function of the independent variables
Transient	Temporal profile of the state variables after a perturbation on the boundary conditions
Boundary conditions	Constraints that apply to the solution of state equations (e.g., initial values, mass balances)
Parameters	Constants in the state equations (constant in a particular case, but may vary in different cases)
Sensitivity coefficient	Partial derivative of a state variable with respect to variations in a parameter
Black box model	A model that is not based on any supposed mechanism
White box model	A model that is based on a supposed mechanism
Gray box model	A model that contains both empirical and mechanistic elements

way to a new steady state. If we were to look only at the two steady states without looking at how the system changes in between, we would lose much information. Relations that describe these changes are very informative. Physical and biological models often arise as solutions of differential equations. Therefore, some knowledge of calculus is needed (more details can be found in Appendix A). Depending on the complexity of the problem at hand, analytical solutions can or cannot be found. If not, one has to resort to numerical solutions, but this is relatively easily achieved with appropriate software packages. Another important factor is that regression models are frequently nonlinear in the parameters, the implications of which are discussed in Chapter 7.

To conclude this chapter, Table 2.1 gives an overview of terminology used with mathematical models.

2.3 Concluding Remarks

This chapter has attempted to put the opportunities and limitations of models in perspective of the scientific method. The most important “take home message” is that models are tools to get a grip on reality, but they are definitely not the truth or reality. Obvious as this may seem, one sometimes gets the impression that researchers prefer models over reality, and this is, of course, a capital sin in modeling. In that sense, data should never be fitted to models as is sometimes stated in literature; it should always be the other way around!

Bibliography and Suggested Further Reading

About Modeling

- Box G.E.P. and Hunter W.G. A useful method for model building. *Technometrics* 4:301–318, 1962.
- Box G.E.P. and Hunter W.G. The experimental study of physical mechanisms. *Technometrics* 7:23–42, 1965.
- Box G.E.P. Science and statistics. *J Am Stat Assoc* 71:791–799, 1976.
- Burnham K.P. and Anderson D.R. Model selection and inference. *A Practical Information-Theoretic Approach*. New York: Springer Verlag, 1998.
- Chatfield C. *Problem Solving*. London: Chapman and Hall, 1995.
- Cullen A.C. and Frey H.C. *Probabilistic Techniques in Exposure Assessment: A Handbook for Dealing with Variability and Uncertainty in Models and Inputs*. New York: Plenum Press, 1999.
- Haefner J.W. *Modeling biological systems. Principles and Applications*. 2nd edn. New York: Springer, 2005.
- Kohn M.C. Use of sensitivity analysis to assess reliability of metabolic and physiological models. *Risk Anal* 22:623–631, 2002.
- Phair R.D. Integrative bioinformatics. Practical kinetic modelling of large scale biological systems. www.bioinformaticsservices.com/bis/resources/cybertext/Ibcont.html
- Ratkowsky D.A. *Handbook of Nonlinear Regression Models*. New York: Marcel Dekker, 1990.
- Tijssens L.M.M., Hertog M.L.A.T.M., and Nicolai B.M. (Eds.). *Food Process Modelling*. Cambridge, United Kingdom: Woodhead Publishing Limited, 2001.
- Vose D. *Risk Analysis: A Quantitative Guide*. Chichester, United Kingdom: Wiley & Sons, 2000.
- Zwietering M.H. and Hastings A.P.M. Modelling the hygienic processing of foods—a global process overview. *TranslChemE* 75(C3):159–167, 1997.

About Ockham's Razor

- Jefferys W.H. and Berger J.O. Ockham's razor and Bayesian analysis. *Am Scientist* 80:64–72, 1992.

3

Chemical Thermodynamics in a Nutshell

3.1 Introduction

Although the topic of this book is on kinetics, we consider it appropriate to include a short chapter on chemical thermodynamics, which is the branch of thermodynamics that studies how chemical reactions come to equilibrium. The reason to do this is that thermodynamics and kinetics are complementary to the study of chemical reactions. Thermodynamic parameters are also used in the formulation of chemical kinetics, as we shall see later on in this book. Thermodynamics is, in short, the science of conversion of energy and matter. Reversible thermodynamics makes statements about systems in equilibrium, and gives an answer to the question: what drives chemical reactions toward equilibrium or to completion? Reversible thermodynamics is reasonably established by now. In contrast, irreversible thermodynamics, which makes statements on processes and systems that are not in equilibrium, is still debated. Most of this chapter will be on reversible thermodynamics, with some remarks about irreversible thermodynamics at the end of the chapter. Irreversible thermodynamics makes a nice link to kinetics. Kinetics gives an answer to the question, how does it happen and at what rate, and that will be addressed in subsequent chapters.

The chapter is organized as follows. Both for thermodynamics and kinetics we need to be able to express quantitatively the progress of a reaction, so we start with a section on how to quantify reactants and products. This is not only needed for this chapter but also for the rest of the book. Then we move to chemical thermodynamics, by first highlighting the concepts of energy, enthalpy, entropy, and free energy. Then we discuss the difference between ideal systems and real, nonideal systems and how we cope with nonideal systems via the activity concept. We continue by considering how these concepts can be used to state something about direction of processes and equilibrium positions of reactions. Finally, we conclude the chapter by making the move from reversible to irreversible thermodynamics, and from there we will make a connection to kinetics.

3.2 Quantification of Reactants and Products

Ways to express amounts and concentrations. The amount of chemicals present in a solution can be expressed in many ways. The chemical present in the highest amount is called the solvent, and the chemical present in lower amount the solute (obviously there can be more than one solute in a solvent),

and the whole of solutes and solvent is called a solution. We will mostly refer to thermodynamics and kinetics in solution, and the most common way to express amounts is then via molarity, i.e., the number of moles of solute per liter of solution. This is indicated by the symbol *M* (molar). Another way is via molality, which is the number of moles of solute per kilogram of solvent, indicated by the symbol *m* (molal). Yet another way is molinity, i.e., the number of moles per kilogram solution, but this unit is hardly ever used. In most cases relevant for foods, the solvent is water. Since the density of water is about 1 kg dm^{-3} , there will not be too much difference between molarity and molality for diluted aqueous solutions. However, it should be realized that it depends on the density of the solution in how far molality and molarity differ, and for foods this can make quite a difference. Also, molarities do depend on temperature because the volume changes with temperature while molalities do not. Furthermore, for some foods, such as cheese, or tomato paste, it is hard to envisage what a liter of solution actually means. So, it would not be a bad idea to use molalities instead of molarities for foods, but it is not very common. Another possible way of expressing amounts is via the mole fraction, i.e., the number of moles of solute divided by the total number of moles present in the system. Mole fractions are mostly used for more concentrated systems, but this unit only makes sense for well defined, simple systems, not for foods. Molarities/molalities are more used for dilute systems. Then, it is of course also possible to express amounts in mass fractions, indicated by the symbol *w/w* (e.g., g solute/kg solution), mass–volume fractions *w/v* (e.g., g solute/L solution), and volume–volume fractions *v/v* (e.g., mL solute/L solution); these are expressed often as percentages, and sometimes also as ppt (parts per thousand, e.g., g solute/kg solution) or ppm (parts per million, e.g., mg solute/kg solution). In this book, we use mostly concentrations expressed as molarity or molality, but occasionally other measures will also be used. In any case, it will always be indicated how amounts are expressed as this is a prerequisite for thermodynamics and kinetics. Of course, the various ways to express amounts can be converted into each other, but extra information may be needed. For instance, to convert molar concentration into molal concentration, the density of the solution is needed. Appendix B gives an overview of ways to express amounts and some formulas for conversions.

To show the intricacies involved for foods, the example of milk is a nice one. A liter of milk is not a pure solution; it also contains fat globules and casein micelles, i.e., these components are not dissolved but dispersed. Lactose is really dissolved and is part of the milk serum (the part of milk that can be considered as aqueous solution). So, the concentration of a solute like lactose can be expressed in several ways, as shown in Table 3.1, and it does make a difference which unit is used to express the amount of lactose present in milk.

Sometimes, components are quantified in solutions that are first separated from a food before the analysis. It may be that the ratio of a component to water in such a separated solution is larger than that ratio in the food from which the solution is obtained. This is due to the phenomenon of steric exclusion, which implies that the volume occupied by one particle is not available for another particle. Solute molecules need to keep a distance from the surface of large particles, and this distance depends on the size of the solute. In other words, a part of the volume is not accessible to solute molecules but is accessible to water molecules: this is the nonsolvent water. Obviously, the effect is larger for larger particles. Figure 3.1 illustrates this effect graphically. Corrections should be applied when concentrations

TABLE 3.1 Various Ways to Express the Amount of Lactose in Full-Fat Milk

Expression	Unit	Result
Mass percentage (%)	g/100 g milk (%)	4.6
Concentration (molinity)	mol kg ⁻¹ milk	0.134
Concentration (molarity)	mol L ⁻¹ milk (M)	0.138
Concentration (molality)	mol kg ⁻¹ water (m)	0.154

Note: 4% fat, 12.8% dry matter, density 1030 kg m^{-3} .

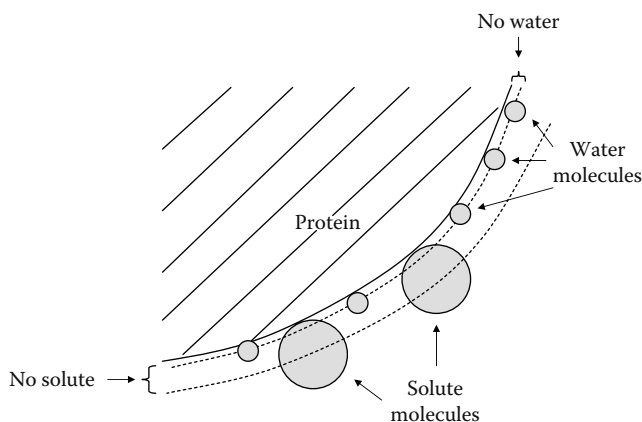


FIGURE 3.1 Graphical illustration of the steric exclusion effect resulting in the presence of nonsolvent water.

determined in a solution obtained from a food are recalculated to the corresponding concentration in the food itself.

Stoichiometry of reactions. In a chemical reaction, molecules interact (react) with each other and the result is the formation of products in which atoms are arranged differently than in the original reactant molecules. When a chemical reaction occurs, the proportions of the amounts of participating molecules change. Suppose we have a reaction represented symbolically as



where ν_A , ν_B , ν_P , ν_Q represent the number of molecules or moles of reactants A and B, and products P and Q, respectively (it is just a convention to call the components on the left-hand side reactants and the ones on the right-hand side products). The equation is a standard notation for a chemical transformation and is called a stoichiometric equation (from the Greek words *στοιχεῖον* [stoicheon], meaning element, and *μέτρον* [metron], meaning measure). The importance of a stoichiometric equation is that it defines the exact change from initial number of molecules to the final composition; in other words, such a change is not arbitrary. The bidirectional arrows indicate that reactants can also be formed from the products, and when there is a balance between formation of products and reactants a steady state is reached, which may or may not be an equilibrium; a more formal definition for equilibrium will be given later on. $\nu_{A,B,P,Q}$ are called the stoichiometric constants, which can be seen as physical quantities representing the change in the number of molecules of a component per chemical transformation as indicated by the reaction equation. They indicate fixed proportions of the number of moles upon chemical transformation. We can generalize Equation 3.1 for more reactions in the following way. Suppose there are n species A_i ($i = 1, \dots, n$) and r independent reactions ($j = 1, \dots, r$). An example is the decarboxylation of amino acids, an important reaction in ripening cheese with respect to flavor development. The following reactions are possible:

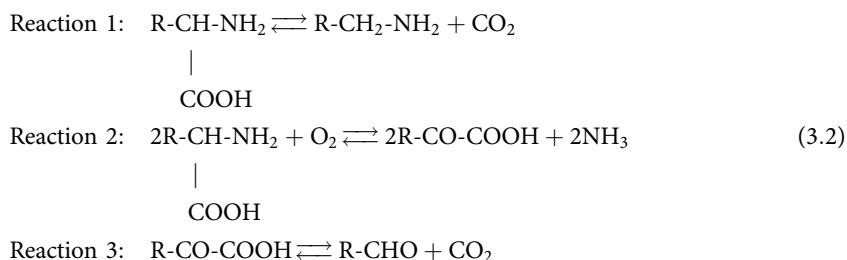


TABLE 3.2 Stoichiometric Table for the Reactions in Equation 3.2

Species <i>i</i> Reaction <i>j</i>	R-CH(COOH)- NH ₂ (<i>i</i> = 1)	O ₂ (<i>i</i> = 2)	R-CH ₂ - NH ₂ (<i>i</i> = 3)	CO ₂ (<i>i</i> = 4)	R-CO- COOH (<i>i</i> = 5)	R-CHO (<i>i</i> = 6)	NH ₃ (<i>i</i> = 7)
<i>j</i> = 1	-1	0	+1	+1	0	0	0
<i>j</i> = 2	-2	-1	0	0	+2	0	+2
<i>j</i> = 3	0	0	0	+1	-1	+1	0

So, we have three reactions ($r = 3$) and seven species ($n = 7$). We can set up a table for the stoichiometric constants (Table 3.2). The convention is that stoichiometric constants are indicated with a negative sign for reactants (because the number of these molecules decreases) and a positive sign for products (because the number of product molecules increases as the reactions starts with reactants A and B).

Such a table can be summarized in the so-called stoichiometric matrix

$$\begin{bmatrix} -1 & 0 & 1 & 1 & 0 & 0 & 0 \\ -2 & -1 & 0 & 0 & 2 & 0 & 2 \\ 0 & 0 & 0 & 1 & -1 & 1 & 0 \end{bmatrix} \quad (3.3)$$

Matrices are just convenient ways to represent a bunch of numbers. A concise way to represent balanced reaction equations such as Equation 3.2 is

$$\sum_{i=1}^n \nu_{ij} A_i = 0 \quad (3.4)$$

In the case of just one reaction, $r = 1$, Equation 3.4 reduces to

$$\sum_{i=1}^n \nu_i A_i = 0 \quad (3.5)$$

A balanced reaction equation such as in Equation 3.1 does not necessarily represent the actual mechanism of a reaction. What it does represent is the proportion in which changes occur in amounts of reactants and products. It is important to be aware of this distinction. It may well be that at the molecular level (i.e., elementary reactions) the reaction depicted in Equation 3.1 is as follows:



A1 and B1 represent transient intermediates that do not appear in the overall stoichiometric equation. An example of such a reactive species is a radical, for instance formed in several oxidation processes in foods. The danger in using an overall reaction equation such as Equations 3.1 and 3.2 is that it represents the final outcome of a reaction. One is, however, not allowed to add up reaction equations (such as Equation 3.6) as if they were algebraic equations. This is especially so for a kinetic treatment: sometimes the intermediates are very important from a kinetic point of view. It can cause much confusion if reaction (Equation 3.1) is taken as the actual mechanism when it only reflects the balance in amounts of reactants and products.

When we want to study how a reaction progresses we are in need of a parameter that describes this progress. Such a parameter is ξ , the extent of the reaction.

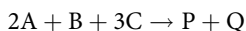
Extent of reaction. With the number of moles expressed as n_i , and $n_{i,0}$ the initial number of moles for component i , the extent of reaction is defined as

$$\xi = \frac{n_i - n_{i,0}}{\nu_i} = \frac{\Delta n_i}{\nu_i} \quad (3.7)$$

or expressed in terms of the number of moles

$$n_i = n_{i,0} + \nu_i \xi \quad (3.8)$$

The stoichiometric constant ν_i indicates the amount of component i in the reaction. ξ is a time-dependent variable describing the advancement of a reaction and is proportional to the net number of transformations in going from left to right in Equation 3.1. ξ could be referred to as the amount of chemical transformations (or number of events) expressed in number of moles. $\xi = 0$ means that the amount of (at least one) product is zero. A maximum value $\xi_{\max}$ is reached when at least one reactant is exhausted; this will happen for a reaction going to completion. The exhausted reactant is called the stoichiometrically limiting reagent. The amount of a limiting component consumed in the reaction must be equal to the amount initially present. The limiting reagent is therefore the component that has the lowest value of $\frac{n_{i,0}}{|\nu_i|}$ and $\xi_{\max}$ is numerically equal to this lowest value (as follows from Equation 3.7). An example may clarify this a bit more. Suppose we have a reaction depicted by:



and the reaction starts with initial amounts as shown in Table 3.3. The limiting reagent for the initial conditions indicated is thus component C.

In the case of a reaction not going to completion, an equilibrium ξ_{eq} will be reached as discussed below in the section on equilibrium. ξ specifies the composition of a reaction mixture during the course of the reaction; it is a useful parameter because it describes the extent of reaction regardless of which compound is considered. It should be realized that ξ can be larger than 1. For more than one reaction ($j = 1, \dots, r$) with n components ($i = 1, \dots, n$), Equation 3.8 becomes

$$n_i = n_{i,0} + \sum_{j=1}^r \nu_{ij} \xi_j \quad (3.9)$$

It is possible to turn the parameter ξ into a dimensionless parameter, for instance by using $\xi_{\max}$

$$\alpha_r = \frac{\xi}{\xi_{\max}} \quad (3.10)$$

α_r is called the degree of reaction, with a numerical value between 0 (only reactants present) and 1 (only products present).

TABLE 3.3 Example of Calculation of $\xi_{\max}$ for the Reaction $2A + B + 3C \rightarrow P + Q$

Component	A	B	C	P	Q
$n_{i,0}$ (mol)	1	1	1	0	0
ν_i	-2	-1	-3	1	1
$\xi_{\max}$ (mol)	1/2	1/1	1/3		

Another frequently used measure for the progress of a reaction is the fractional conversion parameter, f_c

$$f_c = \frac{n_{i,0} - n_i}{n_{i,0}} \quad (3.11)$$

In contrast to ξ , f_c depends on the species i and is related to the extent of reaction as follows (cf. Equations 3.7 and 3.11):

$$\xi = -\frac{f_c n_{i,0}}{\nu_i} \quad (3.12)$$

These parameters are needed to calculate the amounts of reactants and products as a reaction progresses. We will use them in the sections and chapters to follow. Now that we have learned about the parameters needed to express quantities we can turn to thermodynamics and, subsequently, kinetics.

3.3 Thermodynamics of Reactions

Thermodynamics is the science of energy; it includes all aspects of energy and energy transformation and relationships among the properties of matter. For instance, a cup of hot coffee will cool down but it will never reach a higher temperature by itself, and thermodynamics offers an explanation for that. *Thermo* is the Greek word for heat (θερμη), and *dynamics* for power (δυναμις). Chemical thermodynamics is the study of the interrelation of heat with chemical reactions or with a physical change of state. It can provide information about the equilibrium position in a chemical process, i.e., whether or not the reaction can take place when one starts with the reactants A and B, to what extent, and in which direction. The possible exchanges of work, heat, or matter between a system and its surroundings take place across a boundary proceeding from an initial state to a final state. Then, one may want to know how this equilibrium can be influenced by, for instance, temperature and pressure changes. It is for these reasons that we would like to remind the reader of some relevant thermodynamic principles for (chemical) reactions.

3.3.1 Heat and Work

As mentioned, the basic considerations for thermodynamics are heat effects (thermo) and work effects (dynamics). Heat is the reflection of random molecular motion, work is organized motion (force $\times$ distance). Work can appear in various forms: gravitational, expansion, tension, electrical, dissipative force of friction, and also chemical. Heat and work are processes by which energy is transferred between a reactive system and its surroundings. Work is the energy needed to do something. Thermodynamics allows one to account quantitatively for how much energy goes where. In principle, thermodynamics is model independent and does not refer necessarily to molecular events; this model independency is the case of classical thermodynamics. Thermodynamics can be built also upon quantum mechanics and this is called statistical thermodynamics. Statistical thermodynamics determines the distribution of a given amount of energy E of n identical systems. The goal of statistical thermodynamics is to understand and to interpret the measurable macroscopic properties of materials in terms of the properties of their constituent particles and the interactions between them. This is done by connecting thermodynamics functions to quantum mechanic equations. Since it does help in understanding to consider molecules, the discussion given below contains elements of both classical and statistical thermodynamics. It is important to realize that thermodynamics only applies to macroscopic amounts, i.e., large numbers of molecules. Before we discuss some aspects of thermodynamics it may be useful to recall some basic terminology (Table 3.4). The reader is advised that the following thermodynamic considerations are not as rigorous as they perhaps should be. It is not the intention of this book to discuss thermodynamics in great detail; it merely aims to make the link with kinetics. There are many excellent textbooks on the topic and some suggestions for further reading are given at the end of this chapter.

TABLE 3.4 Descriptions of Some Terms Used in Thermodynamics

Term	Meaning
System	Part of the universe that is studied
Surroundings	Part of the universe outside the system
Open system	System can exchange mass and energy with surroundings
Closed system	System can exchange energy with surroundings but cannot exchange mass
Isolated system	System can neither exchange mass nor energy with surroundings
Adiabatic system	System that does not exchange heat with surroundings
Isothermal system	Uniform temperature, i.e., no temperature gradients in the system
Isobaric system	Uniform pressure, i.e., no pressure gradients in the system
Isochoric system	System at constant volume
Diathermic system	System that permits heat transfer
Intensive variable	Does not depend on the amount of the quantity it refers to
Extensive variable	Does depend on the amount of the quantity it refers to
Equilibrium state	No net production or consumption of components (chemical reactions), no unbalanced forces (mechanical), no temperature gradients (thermal)
Spontaneous process	A process that occurs in a system without any work being done on the system
Reversible process	The system as well as the surroundings return into the same state when a process is reversed by infinitesimal changes of a variable
Irreversible process	Net changes in the state of a system and surroundings have occurred as a result of the process that cannot be reversed

System, surroundings, and universe. First of all, we divide the universe into system and surroundings (Figure 3.2). A system can be any part of the universe that we want to study, so it can be a single reaction, an aggregate, an emulsion droplet, a whole food, a food factory, etc. The system and its surroundings are distinguishable because one can imagine some type of boundary between them, and this boundary does or does not permit exchange of matter and energy (see Table 3.4 for the possibilities and the terminologies). For instance, a can containing food can exchange heat with the surroundings but not matter, and canned foods are therefore closed systems. Hot coffee in a closed Dewar flask forms an isolated system (in principle at least, though in practice not completely because eventually the coffee temperature will assume the temperature of the surroundings). Freshly baked bread left on the table is an open system:

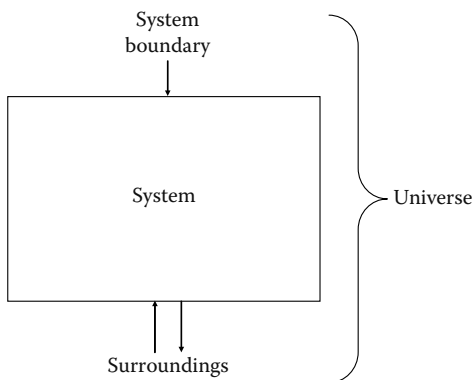


FIGURE 3.2 Schematic representation of the universe and its constituents: a system and its surroundings, separated by a boundary.

there will be exchange of heat (the bread cools down, the surroundings warm up) and of matter (water will evaporate from the bread). Incidentally, these simple examples demonstrate why packaging of foods is so important, because one can influence then the interaction of a food with its surroundings through manipulating the boundaries (gas permeation, solubility of components in the packaging material, etc.), and thereby one can control reactions.

The conditions that describe a system are called collectively the state of the system. A change in conditions implies thus a change of state. Conditions that must be specified to establish the state of a system are called state variables (such as pressure, temperature, volume, number of molecules). An equation of state describes mathematically how state variables are related. A change from one state to another is called a

process. A reversible process in thermodynamic terms is brought about by infinitesimal changes of a variable and it means that going along the same path in reverse restores the system as well as the surroundings to its original state. With irreversible processes, permanent changes have occurred in the system and/or surroundings. This terminology may cause some confusion because a reversible reaction in chemical terms refers to a reaction in which products are formed from reactants but reactants can also be formed from products; an irreversible reaction means essentially that reactants are completely converted into products. The difference is thus in the words “process” and “reaction.” A reversible process does not really occur in nature, it is rather an idealized process, a thought experiment, which is nevertheless useful in practice because it helps in determining the limits of real processes. Real, natural processes are irreversible, though some real processes may approximate reversible processes, such as the melting of ice around 0°C. An important point is, however, that some thermodynamic functions can only be evaluated when considering reversible processes. We describe first classical thermodynamics for reversible processes; at the end of this chapter we will spend some words on irreversible thermodynamics because of its practical importance.

Another important consideration is that of ideality; ideal gases and solutions are characterized by the absence of interactions between molecules. They represent limiting cases of real behavior. For instance, ideal solutions do not show a heat or volume effect upon mixing, whereas real solutions do. This is particularly of importance when trying to describe properties of foods in thermodynamic terms. Foods behave by no means as ideal solutions and gases; they are usually inhomogeneous, concentrated, and show many interactions between components. Ideal solutions and gases could be the starting point to derive trends but one should expect complications when applying such concepts to foods. In this book we consider reactions in foods mainly as if they take place in solution, at least as the reference point, acknowledging however, that solid (e.g., crystals) and gaseous phases (e.g., flavor volatiles in headspaces, bubbles in foam) are also important. We will come back to some specific food complications in Chapter 14.

A physical change of state (such as melting, or expansion) implies that the atoms or molecules involved do not change. A chemical change of state implies that the amounts and identities of reactants and products change, in addition to a possible physical change of state. A system is characterized by intensive and extensive parameters. An intensive parameter (or quantity, variable) such as temperature is independent of the amount of substance in the sample and an extensive parameter such as mass, or volume, or energy does depend on the amount of substance. However, the ratio of two extensive parameters, such as density calculated from the ratio of mass and volume, yields an intensive parameter. When chemical reactions occur it is useful to distinguish between species and components. A component can be the sum of several species. For instance, a salt (the component) can consist of several ions (the species). An important concept in thermodynamics is about state and path functions. State functions describe variables that only depend on the difference between one state or another but not on how the change occurs. Path functions on the other hand describe variables that depend on how the changes have occurred. Heat and work are path functions. Energy is a state function. This brings us to the topic of energy.

3.3.2 Energy

The basic thermodynamic property is the internal energy E . We cannot measure this internal energy in absolute terms, but we can measure energy changes. This is an important point to note because it explains the need for a reference point, and that is why standard states are introduced in thermodynamics. We will come back to this shortly. Energy comes in several forms: kinetic energy (i.e., translational, vibrational, or rotational energy of motion of molecules), potential energy (gravitational, chemical, electrical), thermal energy (characterized by incoherent motion of molecules), radiant energy, and even mass is related to energy according to the Einstein equation $E = mc^2$. In terms of chemical reactions, energy mainly refers to potential and kinetic energy in molecules, namely the bond energies of molecules, and translational, rotational, and vibrational molecular motions, respectively. The forms of energy mentioned are all

interchangeable, and the first law of thermodynamics states that energy is conserved throughout. This means that energy cannot be lost. However, the quality of energy, when expressed as its ability to do work, can diminish, as we will discuss shortly. Exchange of energy between system and surroundings can happen via heat (q), or via work (w); work = force $\times$ distance. There are different kinds of work possible: chemical, mechanical, electrical, and magnetic. A flow of thermal energy is known as heat; thermal energy itself is an energy content. It is important to understand that heat q and work w are modes of energy transfer; they depend on the path the process takes in going from the initial to the final state. This path dependency means mathematically that the integral of the differential of work or heat depends not only on the initial and final states but also on the path connecting them; therefore the differentials are so-called inexact differentials (indicated by the operator D). In contrast, the integral of an exact differential (indicated by the operator d) is independent of the path between initial and final states, and therefore depends only on the initial and final states. The result is a state function. However, the sum of these two inexact differentials is an exact differential. So we should write

$$dE = Dq + Dw \quad (3.13)$$

But when the final state is reached we can write for the change in energy

$$\Delta E = q + w \quad (3.14)$$

Energy of a system depends only on the current state, not on how it reached that state, in other words, the sum of q and w is always independent of the path between a given initial and a given final state. Heat and work relate to processes; the energy content of a system cannot be divided into a heat part and a work part after the process. According to the first law of thermodynamics, the following relation should hold:

$$\Delta E_{\text{system}} = q_{\text{system}} + w_{\text{system}} = -\Delta E_{\text{surroundings}} \quad (3.15)$$

Expressed in words, if the system gains energy the surroundings will lose the same amount of energy and vice versa, and these energy changes are brought about by heat and work. Once again, this refers to changes in energy content (symbolized by the symbol Δ), not to the energy content itself. Once the transfer of energy is completed, the contributions of heat and work are no longer distinguishable. One cannot say that a system contains so much heat or so much work; it only contains energy.

Temperature is not energy but a measure for the average kinetic energy of atoms or molecules. There is a relation between temperature change (ΔT), the amount of heat transferred (q), the amount of material that is involved (N), and the type of material (expressed as molar heat capacity at constant pressure C_p)

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = \frac{q}{NC_p} \quad (3.16)$$

3.3.3 Enthalpy

Most chemical reactions occur at constant pressure, which means that volume changes may occur, so that work is done against the external pressure. For convenience, a new thermodynamic property called enthalpy is defined

$$H \equiv E + PV \quad (3.17)$$

The equation that accounts for changes in enthalpy at constant pressure is

$$\Delta H = \Delta E + P\Delta V \quad (3.18)$$

If the only work done is work against pressure ($w_{\text{system}} = -P\Delta V$, which is negative by convention because the work is done by the system on the surroundings), the combination of Equation 3.18 with Equation 3.15 shows that

$$\Delta H = q_{\text{system}} + w_{\text{system}} + P\Delta V = q_{\text{system}} - P\Delta V + P\Delta V = q_{\text{system}} \quad (3.19)$$

In words, the enthalpy change accounts for the heat flow at constant pressure. Enthalpy is an extensive quantity like energy. Incidentally, volume changes for solids and liquids are usually negligible, so that for these systems $\Delta E \approx \Delta H$. One can calculate enthalpy changes for chemical reactions using tabulated values for known compounds. Since we are interested in differences rather than absolute values, so-called standard states are used as reference points. Standard states refer to the state of an element, of a gas, a solid or a liquid, or a solvent, or a solute, at a pressure of 1 bar.* It is the convention in thermodynamics to assign zero enthalpy to all chemical *elements* (not components!) in their most stable state at 1 bar pressure. It should be realized that this is entirely arbitrary and it is just a matter of agreement. What may be confusing is that standard states for components can be defined in various ways, as we shall see later when discussing chemical potentials. For the moment, let us denote a standard state by the superscript “°,” so that H° indicates the value of the enthalpy at the standard state, for instance of one mole of gas at $P = 1$ bar. Later on we will make a distinction between the various standard states and indicate this also by a different superscript. Next to the standard state, temperature has to be specified, and usually the temperature chosen is 25°C (298.15 K), but again, this is arbitrary (a standard state refers to a concentration or pressure, not to a temperature). The standard reaction enthalpy change $\Delta_r H^\circ$ is thus the change in enthalpy when reactants in their standard states change to products in their standard states (the subscript “r” indicates reaction). Besides reaction enthalpies there are also enthalpies of physical change, for instance, enthalpies of fusion or evaporation. A standard reaction enthalpy covers the overall process from pure unmixed reactants in their standard states to pure separated products in their standard states. A thermochemical equation is a combination of a chemical equation and a standard reaction enthalpy change. Referring to Equation 3.1, a general formula to calculate the standard reaction enthalpy is

$$\Delta_r H^\circ = \nu_P H_P^\circ + \nu_Q H_Q^\circ - \nu_A H_A^\circ - \nu_B H_B^\circ \quad (3.20)$$

where $H_A^\circ, H_B^\circ, H_P^\circ, H_Q^\circ$ are the standard enthalpies of A, B, P, Q per mole, respectively, with the unit of J mol^{-1} . For instance, the balanced chemical equation for the oxidation of glucose is



The difference in enthalpies of reactants and products in their standard state is:

$$\Delta_r H^\circ = (6 \times H_{\text{carbon dioxide}}^\circ + 6 \times H_{\text{water}}^\circ) - (1 \times H_{\text{glucose}}^\circ + 6 \times H_{\text{oxygen}}^\circ) = -2820 \text{ kJ mol}^{-1}$$

The negative sign indicates that the system releases energy when this reaction takes place. This energy was stored as chemical energy in the glucose molecules (it is in fact an exothermic reaction; we will come back to this shortly). Incidentally, this energy was originally captured by plants from sunlight via photosynthesis, and since energy is conserved it can be regained back from glucose. As indicated, the reference state of an element is its most stable state at the specified temperature and at 1 bar and is defined as zero by convention. The standard enthalpy of formation of a substance is the standard reaction

* Many authors use a pressure of 1 atm. According to International Union of Pure and Applied Chemistry (IUPAC) recommendations it should be 1 bar.

enthalpy for the formation of the compound from its elements in their reference states, expressed as enthalpies per mole of compound. Enthalpy changes can be measured as heat exchanges at constant pressure via thermochemical experiments. Also, reaction enthalpies can be calculated from enthalpies of formation $\Delta_f H^\circ$ of reactants and products, which are tabulated for many components

$$\Delta_r H^\circ = \sum_{\text{products}} \nu \Delta_f H^\circ - \sum_{\text{reactants}} \nu \Delta_f H^\circ \quad (3.22)$$

These tabulated values are based on many accurate thermochemical experiments done in the past. Thus, it is now very easy and convenient to calculate enthalpy changes for almost every reaction.

The first law of thermodynamics allows one to calculate energy changes when reactions take place, but there are limitations on the ability to convert heat energy into work. Also, the first law does not indicate the direction of processes: it applies to any process in which energy is conserved, but there is a direction for processes in real life, as is everyone's experience. For example, sugar will dissolve easily in hot coffee, but the reverse process that sugar crystallizes all of a sudden in a hot cup of coffee will not happen (or put more correctly, the probability that this will happen is so extremely low that we can safely state that it will never happen). This is where the second law of thermodynamics comes in: there is a certain direction in which reactions go. In other words, there is a reason why sugar does not crystallize in hot coffee and this reason is called entropy S .

3.3.4 Entropy

Entropy is a rather abstract concept. It is based on the Greek words $\epsilon\nu$ and $\tau\rho\omicron\pi\eta$ (meaning: turning into). It is sometimes referred to as disorder, but this has led to much confusion, and serious misinterpretation. Even though in some limited cases disorder could be a right term, it is preferable and unambiguous to refer to entropy of a system at constant energy as the number of ways energy can be stored in that system; increase of entropy reflects dispersal of energy at some temperature T . So, the entropy of a substance at a temperature T is a measure of the total quantity of energy that had to be dispersed within that substance from $T = 0$ K to T to exist as a solid, or liquid, or gas at that temperature T . With such a notion of entropy, phase changes and colligative properties (such as freezing point depression, boiling point elevation, and osmosis) can be explained. In addition, it also allows us to understand why some reactions occur and others do not, as will be discussed shortly.

The consequence of real-world processes, which are irreversible, is that in every energy transformation the entropy of the universe increases and because of that the potential of the energy available to do work diminishes. So, its "quality" is reduced. Hence, there is a good reason to be careful with the use of energy in society, even though energy cannot be lost according to the first law. A suitable measure for the quality of energy is called exergy, and exergy can be lost. We will not discuss this any further here, except to state that exergy calculations are a useful tool for the food industry to design processes as efficient as possible with regard to energy conversion. The second law of thermodynamics states that there is only one direction for irreversible processes, namely those resulting in an increase in entropy S in an isolated system and the entropy is maximal at the equilibrium state. If changes occur spontaneously (i.e., without any work being done on the system) the total entropy of the system and its surroundings (i.e., of the universe) must increase. This does not mean that the entropy of a system cannot decrease; this actually happens during crystallization or condensation, or in a refrigerator, but the requirement remains that the total entropy of the universe must increase. However, the entropy of an isolated system cannot decrease, as will be made clear shortly. The change in entropy determines whether or not a reaction will occur; the energy changes in a reaction have an effect in as much as they increase or decrease the entropy of the system and its surroundings. The dispersal of energy is the "driving force" for physical as well as

chemical reactions but it is of a probabilistic nature. That means that it is possible for energy to be concentrated temporarily in a system, for instance because there is some barrier that prevent things from happening (otherwise life would not be possible!). This does not conflict with the second law of thermodynamics. We will come back to this when discussing kinetics.

A frequently used term in relation to entropy is spontaneous process (Table 3.4). A spontaneous process is something that occurs without the input of additional energy from outside the system, but there is a direction indicated by entropy, namely the only direction is the one in which the entropy of the universe increases. Although it is not wrong per se to talk about a spontaneous reaction, the adjective spontaneous does not add much. A nonspontaneous reaction does not occur, so the word is actually superfluous. Another possible confusing notion of the word spontaneous is that it should occur immediately, and this is definitely not the case. A spontaneous reaction such as the oxidation of glucose can take a very long time. In equilibrium thermodynamics, time is not a variable.

So far, entropy has been discussed as a qualitative measure, and to make it a quantitative measure, two possibilities exist, in principle at least. The first is to count the number of possibilities for energy dispersal via statistical thermodynamics. From molecular thermodynamics and statistical mechanics, it follows that energies of particles and the probability of position in space are coupled inseparably. Such combinations of energy and space are called microstates. A macrostate is the result of many different microstates of individual particles and a macroscopically observable quantity is an average of these microstates (which depend on the conditions of the system); variables such as temperature, volume, number of molecules, measure a macroscopic state. Microstates are thus quantum mechanical descriptions of the ways that molecules can differ in their energy distribution and probable location. Energy dispersion relates to the way in which the energy of particles (i.e., atoms, ions, molecules) are distributed over vibrational, rotational, and translational energy levels. When particles have the ability to access a higher number of energy levels, they can spread out their energy and as a result the entropy is increased. Hence, the entropy of a macrostate (such as a solution) is a measure of the number of ways in which a system can be different in the energetic distribution of the constituting molecules. The number of possible microstates, Ω , that correspond to a given macrostate is linked to entropy quantitatively via Boltzmann's relationship

$$S = k_B \ln \Omega \quad (3.23)$$

in which k_B is Boltzmann's constant ($1.381 \times 10^{-23} \text{ J K}^{-1}$), and Ω the number of possible microstates. Ω represents the different ways of distributing particle energies over levels leading to the same macrostate. To make this more comprehensible, the following explanation may help. Dispersion of total energy stored in particles is highest when the number of occupied energy levels is as large as possible, while at the same time the distance between the energy levels is as low as possible. Entropy is a measure of the number of occupied energy levels, in other words a measure of the dispersion of energy among accessible microstates. Ω , the number of microstates, is actually the number of possible permutations of the particles while keeping the number of particles the same in the different energy levels

$$\Omega = \frac{(\sum_i n_i)!}{\prod_i n_i!} \quad (3.24)$$

n_i is the number of particles occupying an energy level i . The operator $\prod_i$ represents the continued product: $\prod_i n_i = n_1 \times n_2 \times n_3 \times n_3 \times \dots$. The lowest energy level is most populated, the highest accessible energy level the least. This is quantitatively expressed by the Boltzmann distribution

$$n_i = n_0 \exp\left(-\frac{e_i - e_0}{k_B T}\right) \quad (3.25)$$

where

e_0 is the lowest energy level

n_0 the number of particles occupying energy level e_0

An important effect is the distance between energy levels. If this distance increases, quantum leaps will be larger, energy levels less accessible, and consequently entropy will decrease. The decreased accessibility of the higher energy levels limits the number of microstates. An increase in temperature makes higher energy levels accessible to more particles, which explains why entropy increases with T . It should be clear that there is only one kind of entropy change in a system, namely the spreading of energy among a changed number of accessible microstates regardless whether this is due to a change in volume, composition, or temperature. When processes such as phase transitions and chemical reactions take place, this may result in a change in the number of particles occupying a certain energy level, in a changed accessibility of energy levels, and in a change in distance between energy levels. Figure 3.3 illustrates the number of microstates for 10 particles distributed over 3 and 4 energy levels, respectively, while the distance between the energy levels is kept the same. (Incidentally, Figure 3.3 is inaccurate by depicting only energy levels; quantum levels involve energy as well as position in space and the latter are not shown in the figure.)

Using Equation 3.24 it follows that for the situation in Figure 3.3A the number of microstates $\Omega = 12,600$ while for the situation in Figure 3.3B $\Omega = 3,150$, which implies that the situation depicted in Figure 3.3A is much more probable than the one in Figure 3.3B, in other words the entropy of the system A is much higher than in B. To be sure, the situation depicted in Figure 3.3B is not impossible, but the probability that it occurs is very low. The example of Figure 3.3 is of course purely hypothetical. For real systems, the number of microstates becomes incredibly high and difficult to comprehend, even when expressed logarithmically as in Equation 3.23. This statistical interpretation of the second law leads to the description of an irreversible process as that process that moves the system toward a state of greater probability in the absence of external forces. In reversible processes, the system remains in a state of maximum probability (or very close to it).

A change in entropy between an initial and final state is expressed as

$$\Delta S = k_B \ln\left(\frac{\Omega_{\text{final}}}{\Omega_{\text{initial}}}\right) \quad (3.26)$$

Entropy change is thus expressed as the spreading of energy among a changed number of accessible microstates. This can happen, for instance, due to a change in volume (increased density of microstates),

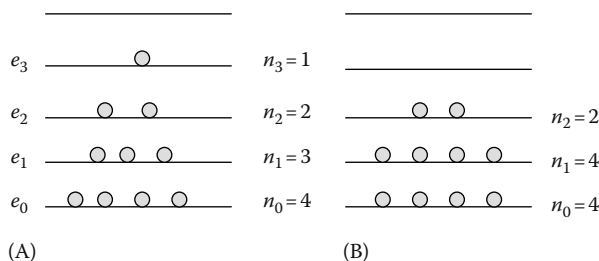


FIGURE 3.3 Schematic depiction of 10 particles occupying energy levels. Higher energy levels ($>e_0$) are less accessible than lower energy levels. The situation depicted in Figure 3.3A is more likely than the one in Figure 3.3B (see text).

composition, or temperature (more energy levels accessible at higher temperature). Boltzmann's formula applies strictly speaking only to isolated systems, and there are some other restrictions as well that we will not discuss here. It suffices here to think of the statistical interpretation of entropy in terms of microstates that belong to the macrostate the system is in.

The second way to look at entropy change is a phenomenological view according to classical thermodynamics, namely by linking the change in energy dispersal to the heat flow between a system and its surroundings. Clausius proposed that for a reversible process a change in entropy is proportional to the heat absorbed and the proportionality constant is $1/T$. As remarked before, heat flow is path dependent and we have to work with inexact differentials (indicated by the operator D)

$$dS = \frac{Dq}{T} \quad (3.27)$$

$1/T$ acts as a so-called integrating factor turning the inexact differential Dq into an exact one for dS . Entropy is thus a state function and we can consider the entropy change ΔS by looking at the difference in initial and final state. Hence, for a heat flow (q) at constant temperature, it follows that the entropy change corresponds to the heat transferred divided by absolute temperature

$$\Delta S \geq \frac{q}{T} \quad (3.28)$$

This is the so-called Clausius inequality. The equality sign ($=$) refers to reversible reactions, the “higher than” sign ($>$) to irreversible reactions. q/T is the entropy change induced in the surroundings by transferred heat. Changes in the entropy function can only be measured along reversible paths. Hence, the entropy change of a reversible process at constant T can be determined from measurements of the heat transferred and the temperature at which this occurs. The entropy change of a system is thus related to the heat transfer by $q/T \leq \Delta S_{\text{sys}}$. For a reversible process $q/T = \Delta S_{\text{sys}}$. For an irreversible process $q/T < \Delta S_{\text{sys}}$ and the heat transfer is less than $T\Delta S_{\text{sys}}$. So, the phenomenological point of view for entropy (as opposed to the statistical mechanical interpretation) is that entropy is a measure of energy degraded during irreversible processes.

For the universe the following relation holds:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} \geq 0 \quad (3.29)$$

If one sums up all of the entropy changes in an isolated system, the entropy change $\Delta S \geq 0$. It is zero if there is equilibrium between all of the subsystems and it is positive when an irreversible change has taken place. Thermodynamic processes which develop so slowly as to allow each intermediate step to be an equilibrium state are said to be reversible processes. In a reversible process the system changes such that the system and surroundings can be put back in their original states by exactly reversing the process. These changes are infinitesimally small. If an irreversible process has occurred the entropy change of the universe must have increased. Statistical mechanics deals with elementary steps which are perfectly reversible. Elementary reactions are reversible. But for a large system, irreversibility becomes important. This is nicely illustrated by looking at the dissolution of a sugar cube in a hot drink. The sugar molecules can in principle move in and out of the crystal lattice in a reversible manner, but the dissolution of the sugar cube as a whole is an irreversible process, because that is the most probable distribution for a large system. We conclude this section on entropy by summarizing the second law in Table 3.5.

TABLE 3.5 Overview of Entropy Changes dS as a Function of Conditions

	Reversible Process	Irreversible Process
Isolated system	$dS = 0$	$dS > 0$
Nonisolated system	$dS = Dq/T$	$dS > Dq/T$

3.3.5 Free Energy

Since the second law reveals the direction of the reaction, namely that which increases the entropy of the universe, we need to be able to calculate this. However, this is an impossible task in terms of the universe. One can get around this problem by defining two other derived thermodynamic quantities called free energy. Free energy can be defined in two ways. At constant volume and temperature we have the so-called Helmholtz free energy F

$$F \equiv E - TS \quad (3.30)$$

At constant pressure and temperature, the so-called Gibbs free energy G is defined as

$$G \equiv H - TS \quad (3.31)$$

We will concentrate here on the Gibbs free energy, but what will follow is valid for the Helmholtz free energy as well. Following Equation 3.31 one can consider the change in Gibbs free energy of a system as follows at constant pressure and temperature

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - \Delta(TS)_{\text{system}} \quad (3.32)$$

Let us now consider a process at constant T so that

$$\Delta(TS)_{\text{system}} = (TS)_{\text{final}} - (TS)_{\text{initial}} = T\Delta S_{\text{system}} \quad (3.33)$$

So, at constant T it follows that

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}} \quad (3.34)$$

Now, when also the pressure is constant $\Delta H_{\text{system}} = q_{\text{system}}$ (cf. Equation 3.19) and $q_{\text{system}} = -q_{\text{surroundings}}$ (Equation 3.15), it follows that

$$\Delta H_{\text{system}} = -q_{\text{surroundings}} \quad (3.35)$$

From Equation 3.28 it follows that for a reversible process $q_{\text{surroundings}} = T\Delta S_{\text{surroundings}}$. Then it also follows that

$$\Delta H_{\text{system}} = -T\Delta S_{\text{surroundings}} \quad (3.36)$$

and now Equation 3.34 can be rewritten, at constant T and P , as

$$\Delta G_{\text{system}} = -T\Delta S_{\text{surroundings}} - T\Delta S_{\text{system}} = -T(\Delta S_{\text{surroundings}} + \Delta S_{\text{system}}) = -T\Delta S_{\text{universe}} \quad (3.37)$$

So, the result of this algebraic exercise is that the change of the Gibbs energy at constant temperature and pressure is the change in free energy of the system and it equals the entropy change of the universe multiplied by the temperature. T and $\Delta S_{\text{universe}}$ can only be positive, hence ΔG_{system} always has to be negative for a process to occur (once again: at constant temperature and pressure). The second law of thermodynamics has been rephrased now in the sense that there is only one direction for processes, namely the direction of decrease in free energy of the system. This is the reason why entropy can never decrease in an isolated system: the entropy of a system can only decrease if energy is put into it and this is not possible for an isolated system by definition (Table 3.4). Upon increase of entropy, energy is still conserved but something is lost (namely part of the capacity to do work; in other words, useful energy is converted into less useful energy) and this is associated with the increase in entropy (namely $T\Delta S$). Thus, entropy change is a convenient measure of the loss of capacity of the system to do work. This all means that if we can measure this free energy change, we can state something about the direction of a process. Equation 3.34 is a very important equation because we now have a tool to calculate whether or not a reaction will take place, provided of course that we can calculate free energy changes.

ΔG is a state function. We are interested in changes, and standard states are also defined for free energies, so the molar standard free energy change ΔG° can be calculated from the standard values of enthalpy and entropy for a particular change

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3.38)$$

Reactions in the nonstandard state. Of course, reactions do not always occur under standard conditions, and if a reaction cannot occur under standard conditions, it may take place under nonstandard conditions (e.g., by changing concentrations and/or temperature). Therefore, one must determine how ΔG depends on temperature and concentration under nonstandard conditions. This can be done as follows. At higher temperature, energy can be dispersed over more levels, so entropy is clearly temperature dependent. However, temperature affects entropies of reactants and products roughly in the same way, so the effect of temperature on the entropy change $\Delta_r S$ due to a reaction is usually small. This means that $\Delta_r S$ can be considered independent of temperature. For the same reason, $\Delta_r H$ can be considered also independent of temperature. Thus, to account for a temperature different from the one specified for the standard condition while keeping the concentration at standard condition, this can be calculated as

$$\Delta_r G_T^\circ \approx \Delta_r H_{T=298\text{ K}}^\circ - T\Delta_r S_{T=298\text{ K}}^\circ \quad (3.39)$$

The next step is to account for a concentration different from standard conditions. As it happens, ΔH° depends hardly on concentration, but entropy does: a more dilute sample has a larger entropy because of more accessible translational energy levels. This can be expressed as a function of pressure as

$$S = S^\circ - R \ln \frac{P}{P^\circ} \quad (3.40a)$$

in which $P^\circ = 1$ bar (standard pressure). A similar equation holds for the dependence of entropy on concentration

$$S = S^\circ - R \ln \frac{c}{c^\circ} \quad (3.40b)$$

where

c is the molar concentration

c° is the unit standard concentration (chosen as 1.0 whichever unit is chosen)

R is the gas constant

Since P° and c° have by definition a numerical value of 1, they are usually omitted; however, it should be realized that c must be expressed in the same units as the chosen standard concentration in order to cancel units. So, for the free energy change under nonstandard conditions Equation 3.34 changes to

$$\begin{aligned}\Delta_r G &= \Delta H^\circ - T\Delta_r S \\ &= \Delta H^\circ - T(\Delta S^\circ - R \ln c) \\ &= \Delta H^\circ - T\Delta S^\circ + RT \ln c \\ &= \Delta_r G_T^\circ + RT \ln c\end{aligned}\quad (3.41)$$

To summarize, if concentrations do not refer to the standard state at the specified temperature, free energy calculations must be done in two stages. First, one has to correct for the temperature being different from the specified one (usually 298 K), using Equation 3.39 to obtain $\Delta_r G_T^\circ$, and then that result can be used in Equation 3.41. These equations show clearly that $\Delta_r G$ depends on concentration as well as on temperature, and this implies that the direction of a reaction can be manipulated by manipulating temperature and concentration. In this respect, it is instructive to consider both enthalpy and entropy changes. If the reaction enthalpy is negative, implying heat transfer from the system to the surroundings, this is called an exothermic reaction. If the reaction enthalpy is positive, this implies a heat flow from the surroundings to the system, and then it is called an endothermic reaction. An endothermic reaction is only possible if the change in reaction entropy is positive. So, for a reaction as depicted in Equation 3.1 the possibilities are as shown in Table 3.6.

An irreversible adiabatic process (no heat exchange between system and surroundings, see Table 3.4) necessarily leads to an increase in entropy of the system in which the process takes place. The tendency of increasing entropy in a given system can be counteracted by putting energy into that system. The total energy of the system plus surroundings remains, of course, constant (first law) and the total entropy increases (second law), but the entropy of the system receiving the energy may increase, decrease, or remain constant. If the entropy change of the system is negative, the system must lose heat such that the entropy of the surroundings increases by at least the same amount; in that case the process is necessarily exothermic. If the entropy change of the system is positive the system can absorb heat such that the decrease in entropy of the surroundings matches the increase in the system; the chemical process can then be either exothermic or endothermic. It is thus possible that an endothermic reaction proceeds, if the gain in entropy (dispersal of energy) is sufficient. This gain in entropy in the system is able to overcome the loss of entropy in the surroundings brought about by the influx of heat (or other forms of energy, such as electric energy) from the surroundings into the system.

For the sake of completeness we also mention the third law of thermodynamics which states that the entropy of a perfect crystal would be zero at 0 K, where all motion would cease. This gives a reference point to calculate absolute entropy values.

Both the Gibbs and Helmholtz energy are defined in terms of the entropy function, implying that they must be evaluated along reversible paths via reversible processes. For most reactions in foods, the

TABLE 3.6 Direction of a Reaction $A + B \rightleftharpoons P + Q$ as Dictated by Values of ΔH , ΔS , and the Resulting ΔG^a

ΔH	ΔS	ΔG
Negative (exothermic)	Positive	Always negative: reaction from left to right at all temperatures
Negative (exothermic)	Negative	Negative at low temperature: reaction from left to right Positive at high temperature: reaction from right to left
Positive (endothermic)	Positive	Positive at low temperature: reaction from right to left Negative at high temperature: reaction from left to right
Positive (endothermic)	Negative	Positive at all temperatures: reaction only from right to left

^a Referring to the reaction going from left to right.

differences between using the Gibbs or Helmholtz free energy will be small. We will use mainly Gibbs energy in this book.

The Gibbs free energy change in a reversible process at constant temperature and pressure equals the work done exclusive of PdV work. It thus represents the maximum quantity of useful energy from a chemical reaction at constant temperature and pressure in a reversible process, and the Helmholtz free energy that at constant volume; useful energy means interconvertible energy (electrical, chemical, mechanical). If there is excess of free energy, or if the free energy cannot be harnessed as useful energy, the free energy represents the maximum extent of energy dispersal to the universe.

Gibbs energy and dissolution. Before considering reactions in more detail, it is also of interest to consider what happens when a compound dissolves in a solvent. For foods, the solvent water is the most important one. The dissolution can be in principle endothermic, exothermic, or a-thermic. It all depends on changes in interactions between solute–solute molecules, solute–solvent molecules, and solvent–solvent molecules. For instance, the dissolution of a crystal depends on the decrease in enthalpy when solvation occurs and the increase in enthalpy needed to disrupt the solvent structure and possibly enthalpy effects of dissociation in the case of electrolytes. Table 3.7 gives a few examples.

Table 3.7 shows that the dissolution of NaCl in water is endothermic but with a positive entropy change. The dissolution of CaCl_2 on the other hand is exothermic but it leads to a negative entropy change. In both cases the Gibbs energy is negative, indicating that dissolution is possible under these conditions. At temperatures higher than 25°C , NaCl would have a greater tendency to dissolve and CaCl_2 less, whereas at lower temperatures the opposite is the case.

To conclude this section, two remarks must be made.

1. Being state functions, changes in ΔE , or ΔH , or ΔS , or ΔG , or ΔF , can be added. However, this can only be done for processes that are independent. This is a requirement that may not always be easy to realize in practice.
2. It should be realized that variables such as enthalpy, entropy, Gibbs, and Helmholtz energies describe huge numbers of particles; these variables do not have any meaning at the level of the individual particles.

3.3.6 Chemical Potential

Every substance has the tendency to change, that is to say, it can

- React with other substances
- Transform into another state of aggregation
- Migrate to another place

This tendency is described by a single physical quantity, the chemical potential μ . Its value depends on a specific substance; it also depends on T , P , and in solution also on concentration and the kind of solvent, and the state of aggregation. So, when we want to evaluate chemical reactions in thermodynamic terms, the chemical potential of components is a very useful concept. In general, a potential indicates the ability

TABLE 3.7 Examples of Standard Molar Enthalpies, Entropies, and Gibbs Energy of Solution in Water at 25°C

Compound	$\Delta_{\text{sol}}H^\circ$ (kJ mol $^{-1}$)	$\Delta_{\text{sol}}S^\circ$ (J mol $^{-1}$ K $^{-1}$)	$\Delta_{\text{sol}}G^\circ$ (kJ mol $^{-1}$)
NaCl	3.89	43.1	−8.9
CaCl_2	−81.3	−44.8	−67.9
CH_3OH (methanol)	−7.28	6.3	−9.2
$\text{C}_2\text{H}_5\text{OH}$ (ethanol)	−10.6	−12.1	−7.0

to do something, and a chemical potential indicates the ability for a component to react, or to move to another phase, etc. The chemical potential μ of a pure substance is defined at constant temperature and pressure as

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{T,P} \quad (3.42)$$

This shows the chemical potential to be the molar Gibbs energy, i.e., it shows how the Gibbs free energy changes as a function of the change in number of moles at constant temperature and pressure. Using Equations 3.40a and 3.37, it can be shown that the following relation holds

$$G = G^\circ + RT \ln \left(\frac{P}{P^\circ} \right) \quad (3.43)$$

As remarked before, thermodynamic quantities can be evaluated only relative to different states, so we need a reference, which is called the standard state, at which G° in Equation 3.43 is evaluated. For a perfect gas, this is the state at which P° is the standard pressure of 1 bar. In a perfect gas there are no intermolecular interactions; the pressure is purely the result of kinetic energy of the molecules. It follows then that for a perfect gas

$$\mu = \mu^\circ + RT \ln \left(\frac{P}{P^\circ} \right) \quad (3.44)$$

μ° is the chemical potential of the component in its standard state.

Moving on now to liquids, imagine a pure liquid compound i that is in equilibrium with its vapor having a vapor pressure P^* . The chemical potential of i in the vapor phase is then (with (g) indicating the gaseous state)

$$\mu_i^*(g) = \mu_i^\circ(g) + RT \ln \left(\frac{P^*}{P^\circ} \right) \quad (3.45)$$

The superscript “*” indicates that we are dealing with the pure compound. At equilibrium the chemical potential of component i in the vapor phase (g) must be equal to that of the component in the liquid phase (l): $\mu_i^*(l) = \mu_i^*(g)$, hence Equation 3.45 can be written also as

$$\mu_i^*(l) = \mu_i^\circ(g) + RT \ln \left(\frac{P^*}{P^\circ} \right) \quad (3.46)$$

Imagine now that component i is not present as a pure compound but is one of the components in a binary liquid mixture causing a partial vapor pressure P_i . Equation 3.45 can then be written as

$$\mu_i(g) = \mu_i^\circ(g) + RT \ln \left(\frac{P_i}{P^\circ} \right) \quad (3.47)$$

Again, at equilibrium $\mu_i(l) = \mu_i(g)$, hence

$$\mu_i(l) = \mu_i^\circ(g) + RT \ln \left(\frac{P_i}{P^\circ} \right) \quad (3.48)$$

By eliminating $\mu_i^o(\text{g})$ from Equations 3.46 and 3.48 it follows that

$$\mu_i(\text{l}) = \mu_i^*(\text{l}) + RT \ln \left(\frac{P_i}{P_i^*} \right) \quad (3.49)$$

We now have an equation that describes the chemical potential of a component in a liquid mixture as a function of vapor pressures. The next step is to connect this to the composition of liquid mixtures. We can do this via the concept of ideal solutions.

3.3.7 Ideal Solutions

As shown, thermodynamic relations are frequently based upon ideal gases. When discussing equilibria in liquid mixtures, it is necessary to know how the chemical potential of a compound in a solution varies with composition. We can make a link between solutions and gases via Raoult's law, which is formulated as follows for each component i :

$$P_i = X_i P_i^* \quad (3.50)$$

P_i is the partial vapor pressure of compound i present in the solution at mole fraction X_i and P_i^* is the vapor pressure of pure compound i . If the total vapor pressure of a solution is the sum of the partial pressures related to mole fractions in solution as expressed by Raoult's law, we speak of an ideal solution. Figure 3.4 shows Raoult's law graphically.

Substituting Equation 3.50 in Equation 3.49 results in the following equation:

$$\mu_i(\text{l}) = \mu_i^*(\text{l}) + RT \ln X_i \quad (3.51)$$

This equation describes the dependence of the chemical potential of component i in an ideal solution on its composition expressed as mole fraction, which is what we were looking for.

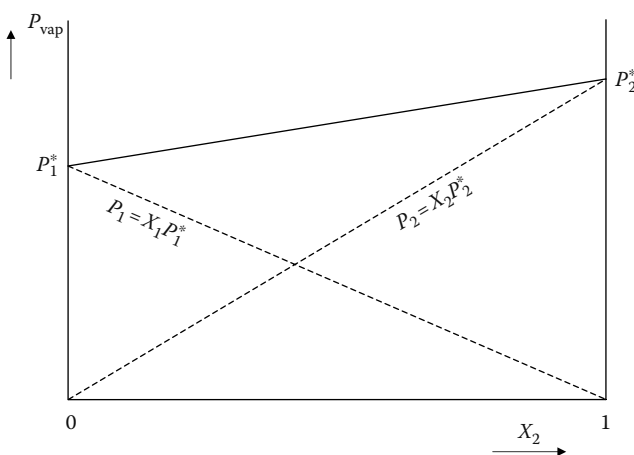


FIGURE 3.4 Illustration of the vapor pressure P_{vap} above an ideal solution consisting of components 1 and 2 as a function of mole fraction X_2 . The solid line represents the vapor pressure of the vapor in equilibrium with a liquid mixture of components 1 and 2. The broken lines indicate the partial vapor pressures of components 1 and 2 according to Raoult's law.

Even though only very few mixtures behave as ideal solutions, they are the starting points to describe the behavior of real mixtures. An ideal solution does not have the same properties as a perfect gas. In a perfect gas, there are no interactions between molecules. In an ideal solution, there is interaction between molecules, but on average the interaction between the solute–solvent, solvent–solvent, and solute–solute molecules are the same as in the pure liquids. In an ideal solution there are no volume and heat effects upon mixing, i.e., $\Delta_{\text{mix}}V=0$ and $\Delta_{\text{mix}}H=0$. For the entropy change $\Delta_{\text{mix}}S$ of mixing in an ideal solution the following relation holds:

$$\Delta_{\text{mix}}S = -R \sum X_i \ln X_i \quad (3.52)$$

This shows that the mixing entropy is always positive for an ideal solution. If a solute at mole fraction X_2 is dissolved in a liquid with mole fraction X_1 , then in an ideal solution the following relation holds (known as the Hildebrand equation):

$$-R \ln X_2 = \Delta_{\text{fus}}H_2 \left(\frac{1}{T} - \frac{1}{T_{\text{fus},2}} \right) \quad (3.53)$$

The subscript “fus” indicates fusion. Likewise, for an ideal solution of a gas in a liquid the following holds:

$$-R \ln X_2 = \Delta_{\text{vap}}H_2 \left(\frac{1}{T_{\text{vap},2}} - \frac{1}{T} \right) \quad (3.54)$$

The subscript “vap” indicates evaporation. As shown, these relations are independent of the solvent in an ideal solution.

3.3.8 Ideal Dilute Solutions

There are solutions in which at very low concentrations of the solute (i.e., $X_1 \approx 1$, $X_2 \ll X_1$) the solvent follows Raoult’s law whereas the solute does not. Figure 3.5 shows this graphically.

The consequence is that in a very dilute solution Equation 3.51 is still valid for the solvent and this is very useful for calculating colligative properties of such solutions (such as freezing point depression, boiling point elevation, osmotic pressure). It can also be observed that for the solute at very low concentrations a linear relationship exists between partial vapor pressure and mole fraction of the solute, be it that this relation is not obeying Raoult’s law. Rather it is following Henry’s law. This implies that the proportionality constant is not the vapor pressure of the pure solute but an empirical constant with the dimension of pressure, called Henry’s constant k_{H} and Henry’s law reads thus

$$P_i = k_{\text{H},i}X_i \quad (3.55)$$

When such a situation occurs, this is called an *ideal-dilute solution*. It can be proven that if the solvent obeys Raoult’s law in diluted binary solutions (say at X_s from 0.9 $\rightarrow$ 1.0) then the solute must obey Henry’s law in that same concentration range, but we will not give this derivation here. A qualitative explanation why the solvent should obey Raoult’s law and the solute Henry’s law is the following. In very dilute solutions, the solvent molecules are almost completely surrounded by other solvent molecules, and therefore they behave as in the pure liquid. However, the solute molecules are surrounded only by solvent molecules in very dilute solutions, and therefore their properties are not the same as in the pure liquid or solid state of the solute. Raoult’s law can actually be seen as a special case of Henry’s law, such that $k_{\text{H},i} = P_i^*$. As mentioned, ideal solutions hardly exist but ideal-dilute solutions do. An example of an ideal-dilute solution is a mixture of water and a little ethanol.

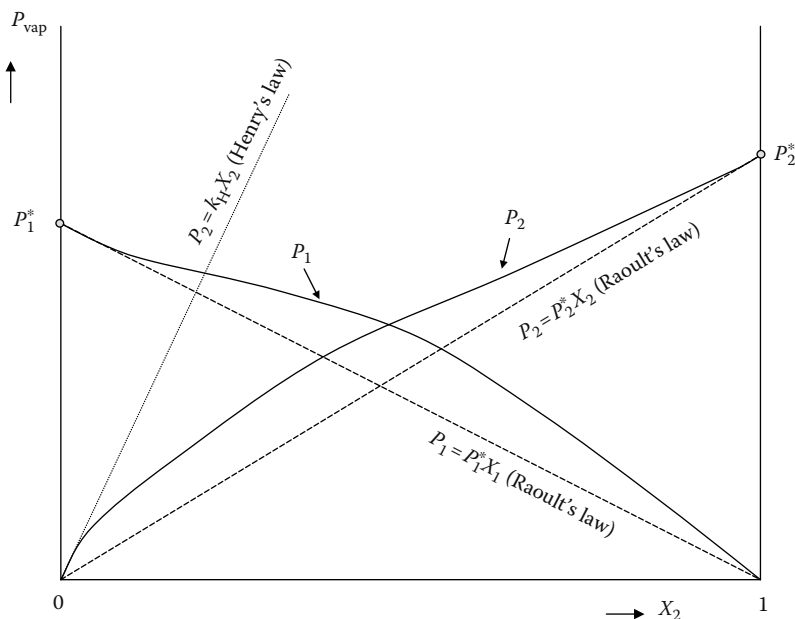


FIGURE 3.5 Behavior of an ideal-dilute solution. Component 1 represents the solvent, component 2 the solute. Vapor pressure P_{vap} and partial vapor pressures P_1 and P_2 are shown as a function of X_2 , the mole fraction of component 2.

3.3.9 Real, Nonideal Solutions: Activity Concept

In real solutions, there may be heat and volume effects upon mixing and there are specific interactions between molecules. Consequently, Raoult's law and Henry's law may not be valid (except for dilute solutions as discussed in the previous paragraph). In order to apply thermodynamic concepts to real solutions, we have to take deviations from ideal solution behavior into account. Figure 3.6 shows two examples of deviations from ideality, one with a positive deviation from Raoult's law (ethanol–water mixture) and one with a negative deviation (glycerol–water mixture). It can be seen that at $X_W \approx 1$ Raoult's law is indeed obeyed if we consider water as the solvent. It can be seen also that the deviation from Raoult's law starts at much higher values of X_1 in the case of ethanol–water mixtures than in the case of glycerol–water mixtures, an illustration of the fact that there are no general rules to predict deviations from ideal solutions.

How can we cope with such deviations? This is done by introducing the concept of activity.* The form of Equation 3.51 is preserved but instead of the mole fraction the activity a_i is introduced (dropping now, for the sake of readability, the (l) notation in Equation 3.51 which indicated that we are dealing with liquids)

$$\mu_i = \mu_i^* + RT \ln a_i \quad (3.56)$$

a_i is a dimensionless quantity, and can be determined experimentally by measuring vapor pressures, because comparison of Equation 3.56 with Equation 3.49 shows that

* For gases, the concept is fugacity, but we will not discuss that here, also because it is frequently assumed that vapors behave as perfect gases

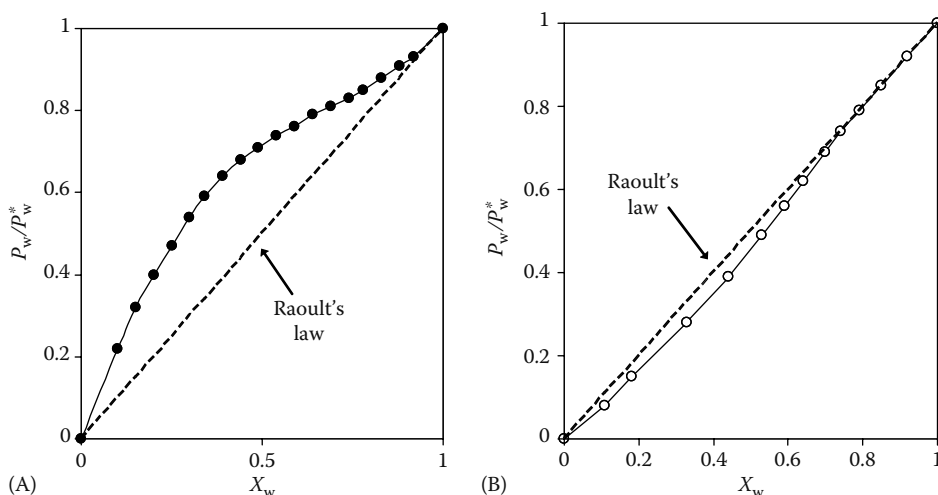


FIGURE 3.6 Examples of deviations from Raoult's law. The ratio of the partial water vapor pressure P_w and the saturated vapor pressure P_w^* is expressed as a function of the mole fraction of water X_w for (A) ethanol–water mixtures (●) and (B) glycerol–water mixtures (○). Data set in Appendix 3.1, Table A.3.1.

$$a_i = \frac{P_i}{P_i^*} \quad (3.57)$$

This equation is valid regardless whether it is an ideal or a real solution. Activity is formally defined as the ratio of the partial vapor pressure of a component in solution and the vapor pressure in the corresponding standard state (strictly speaking these should be fugacities rather than pressures but we will neglect this, so we are in fact assuming ideal behavior in the vapor phase). Thus, it follows from Equation 3.57 that the parameter displayed at the y-axis in Figure 3.6 is the activity of the component displayed (water in Figure 3.6); it is actually water activity, much used in food science, and discussed in more detail in Section 3.3.11 and in Chapter 14.

For a pure compound the standard state is the pure liquid so that $P_i^o = P_i^*$. Figure 3.7 may illustrate the activity concept in more detail. We are in fact using Raoult's law as a reference. The activity is defined as

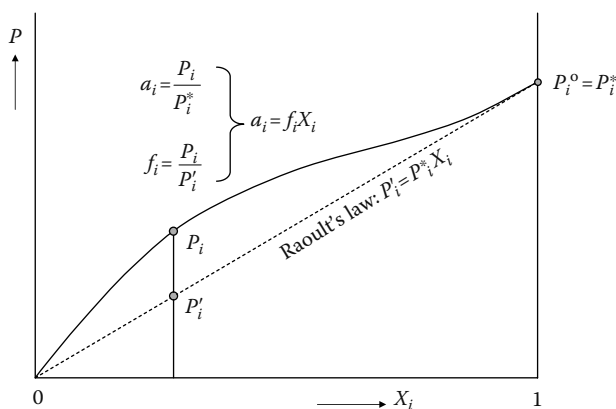


FIGURE 3.7 Hypothetical example of a component in a mixture obeying Raoult's law at $X_i \rightarrow 1$. Schematic illustration of the concept of activity and activity coefficient, using Raoult's law as the reference.

P_i/P_i^* , following Equation 3.57, and to connect the real vapor pressure P_i to the reference value P_i' , as given by Raoult's law ($P_i' = P_i^* X_i$), the activity coefficient is defined as

$$f_i = \frac{P_i}{P_i'} = \frac{P_i}{P_i^* X_i} \quad (3.58)$$

The activity coefficient f_i refers to the mole fraction scale, and is sometimes called the rational activity coefficient. Combining this with Equation 3.57 results in

$$a_i = \frac{P_i}{P_i^*} = \frac{f_i P_i^* X_i}{P_i^*} = f_i X_i \quad (3.59)$$

It should be clear that f_i does not have a constant value in real solutions but varies with composition.

An activity coefficient <1 indicates that the molecules have a preference for the solution over the vapor phase, more than expected on the basis of ideal behavior, while an activity coefficient higher than 1 indicates a preference for the vapor phase (the latter case would be true for the situation depicted in Figure 3.6A). When the mole fraction of a component i approaches 1 ($X_i \rightarrow 1$) in a real solution, its activity coefficient also approaches 1 ($f_i \rightarrow 1$), so that the activity of a component equals its mole fraction. It should be realized that it is just a matter of convention to define activity coefficients in this way. The case of $f_i \rightarrow 1$ when $X_i \rightarrow 1$ is called the symmetrical convention. This convention is most useful for the solvent in diluted solutions. To be sure, for an ideal solution $a_i = X_i$ and consequently $f_i = 1$ over the whole composition range.

So, we have found a way to deal with the solvent in real solutions. What about the solute in a dilute solution? We have seen that in an ideal-dilute solution Henry's law is obeyed for the solute, giving a relation between vapor pressure and mole fraction. Figure 3.8 shows this in more detail.

The activity is defined as

$$a_i = \frac{P_i}{k_{H,i}} \quad (3.60)$$

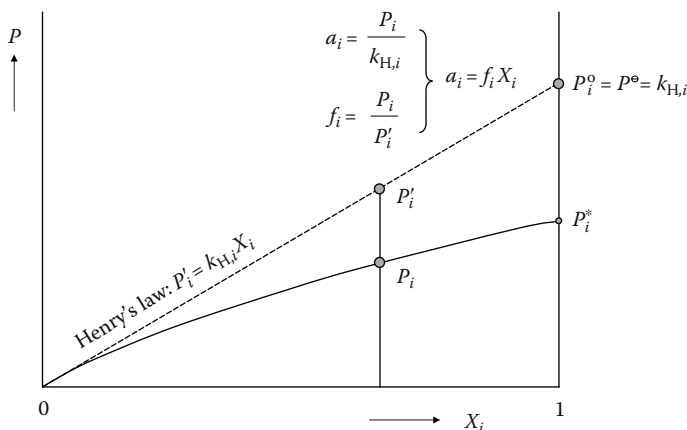


FIGURE 3.8 Hypothetical example of a component in a mixture obeying Henry's law at $X_i \rightarrow 0$. Schematic illustration of the concept of activity and activity coefficient, using Henry's law as the reference.

The activity coefficient is

$$f_i = \frac{P_i}{P_i^*} = \frac{P_i}{k_{H,i}X_i} \quad (3.61)$$

and it follows therefore that

$$a_i = f_iX_i \quad (3.62)$$

The difference with Equation 3.58 is that now $f_i \rightarrow 1$ when $X_i \rightarrow 0$. Once again, this is just a convention and in this case it is called the unsymmetrical convention. In deriving this relation, we have defined Henry's constant $k_{H,i}$ as corresponding to a vapor pressure at the standard state $X_i = 1$ (see Figure 3.8). Even though this is a hypothetical state (because it is extrapolated from the behavior at infinite dilution and does not correspond to the actual vapor pressure P_i^* at $X_i = 1$), this is a valid standard state. This hypothetical standard state is usually indicated by the symbol “plimsoll”[⊖] to indicate the difference with the standard state of the pure compound indicated by the superscript *, as shown in Figure 3.8. So, we managed to deal also with the behavior of a solute in a real, nonideal-dilute solution.

However, the mole fraction is not always a useful concentration measure, unless it is about binary mixtures. Measures such as molarity and molality are more convenient in most practical situations. So, what happens if we want to use, for instance, molality? Figure 3.9 shows again in more detail how we can deal with such a situation. Henry's law is expressed as a linear relation between partial vapor pressure and molality rather than mole fraction, but the standard state is now taken at a molality $m_i = 1 \text{ mol kg}^{-1}$ solvent. Again, this is a hypothetical state because it is extrapolated from the behavior at infinite dilution. The activity is by definition

$$a_i = \frac{P_i}{k_{H,i}} \quad (3.63)$$

The molal activity coefficient γ_i is

$$\gamma_i = \frac{P_i}{P_i^*} = \frac{P_i}{k_{H,i}m_i} \quad (3.64)$$

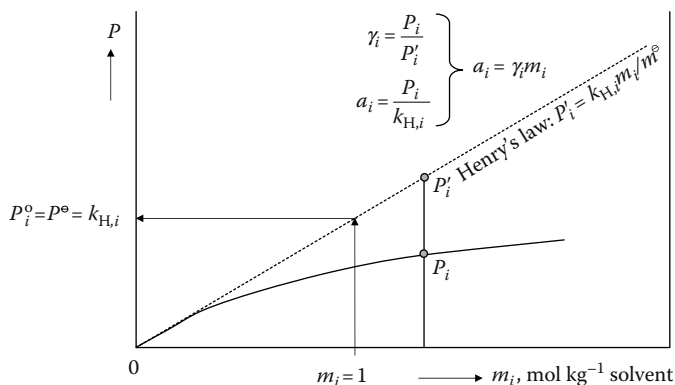


FIGURE 3.9 Hypothetical example of a component obeying Henry's law when $m_i \rightarrow 0$. The standard state is defined at molality $m_i = 1 \text{ mol kg}^{-1}$ solvent extrapolating from ideal-dilute behavior. The corresponding partial vapor pressure is $P^{\circ} = P^{\ominus} = k_{H,i}$.

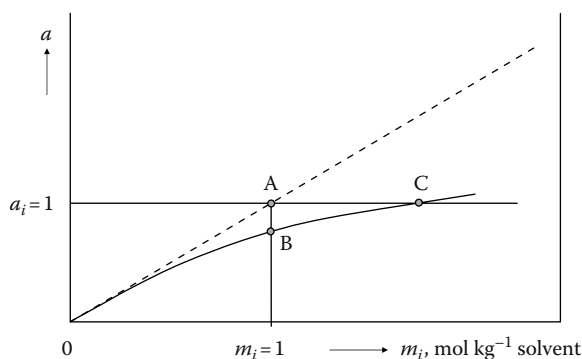


FIGURE 3.10 Graph of a hypothetical situation showing activity of a component as a function of its molality. Point A represents the standard state, points B and C do not (see text).

Consequently, the relation between activity and molality is simply

$$a_i = \gamma_i m_i \quad (3.65)$$

Exactly the same relation can be derived when we take molarity rather than molality by changing m_i to c_i . To differentiate between a molal and a molar activity coefficient the symbol γ_i is commonly used for the molar activity coefficient.

As shown, hypothetical standard states were needed to deal with practical situations. The concept of hypothetical standard states may seem strange at first sight, but to refer the properties of the solute to its behavior at infinite dilution gives a reasonable reference state. This reference state should be seen as a solution for which the concentration term is unity and whose properties are those of an infinitely dilute solution for which the activity coefficient is also unity. However, an activity of unity does not automatically imply a standard state. Figure 3.10 summarizes the possibilities. Point A represents the standard state: both the molality and activity are unity in this point (and hence the activity coefficient as well). Point B is not the standard state: even though the molality is unity, the activity is not. Point C is not the standard state: even though the activity is unity, the activity coefficient is not.

Figure 3.11 gives some examples of activity coefficients for amino acids in water on molality basis. Not unexpectedly, the more hydrophobic amino acids show activity coefficients higher than 1 while the hydrophilic ones have activity coefficients lower than 1. Many empirical models are available in literature describing activity coefficients as function of conditions such as temperature and ionic strength, but we do not discuss them here.

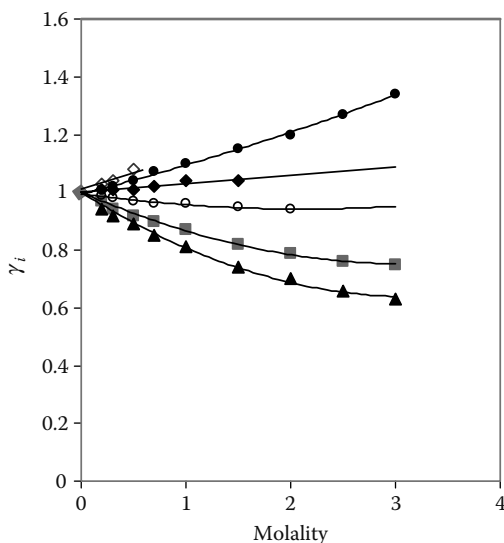


FIGURE 3.11 Molal activity coefficients γ_i for some amino acids in aqueous solutions as a function of their molality: valine ($\diamond$), proline ($\bullet$), alanine ($\blacklozenge$), threonine ($\circ$), glycine ($\blacksquare$), serine ($\blacktriangle$). The lines are just to guide the eye. Datasets in Appendix 3.1, Table A.3.2.

The activity of a component can be regarded as its effective concentration relative to its standard state. It is important to be aware of the fact that activity is defined only in as far as the standard state to which it refers is specified. As we will see especially in Chapters 6 and 14, the activity of a component may differ greatly from its concentration, due to interactions between molecules. The activity coefficient is a quantitative measure for this interaction.

3.3.10 Standard States

To recapitulate, standard states can be chosen arbitrarily and they do not always correspond to experimental attainable conditions. A standard state refers to a concentration (or pressure) at which all the thermodynamic functions have their standard values. The standard state is chosen such that the magnitude of the composition measure (pressure, mole fraction, molality, molarity) equals unity. This becomes clear from Equation 3.56 that can be rearranged to

$$\ln a_i = \frac{\mu_i - \mu_i^\circ}{RT} \quad (3.66)$$

In the standard state $\mu_i = \mu_i^\circ$ by definition, so that $\ln a_i = 0$ and $a_i = 1$. Temperature must also be specified when referring to a standard state, and usually, but not necessarily, a temperature of 25°C is chosen: standard states can be defined at any temperature. So, another way of defining standard states is stating that standard states specify the conditions for which the activities of components equal 1. For a gas, the standard state chosen is an ideal gas at a partial pressure of 1 bar (10^5 Pa). For a real gas, it is the partial pressure of 1 bar of a gas that behaves in the state it would have when $P \rightarrow 0$ (which is a hypothetical state corresponding to a perfect gas). For pure liquids and solids, the standard state chosen is the pure component at a pressure of 1 bar. For solutions we have a convention for the solvent (the state of the pure solvent) and a different one for the solute (the state extrapolated from behavior at infinite dilution according to Henry's law). So, as it happens, we are free to choose any standard state we want, but the choice we make has its bearings on the activity scale. Even though the choice for a standard state is arbitrary, the value of the chemical potential is unique for a certain condition and should of course not depend on an arbitrarily chosen standard state. So, the value of the activity does depend on the choice for a standard state, but the chemical potential does not. Activities can be seen as fictitious concentrations that give the right chemical potential when substituted in the thermodynamic equations. Therefore, it should always be mentioned which standard state is chosen.

Biochemists use still a different state because the activity of H^+ ions in the standard state would be 1.0, and this corresponds to a pH of 0, which is not very realistic in biochemical conditions. Therefore, the standard state for H^+ is changed to pH 7 and this is commonly indicated by a prime, e.g., $\Delta G^{\circ'}$. Table 3.8 summarizes the possibilities. In principle, we could have used different symbols for each condition, for instance, by indicating a_i^x for activity related to mole fractions, or a_i^m for activities related to molality, but that makes equations cluttered and unreadable. It should be clear from the context where symbols refer to and if not, it should be specified. As shown, there are several possibilities to express activities and the reader may wonder if and how values of activity coefficients can be converted into each other. The answer is yes and how this can be done is shown in Appendix C.

It is important to note that especially in food, with its complicated composition and structure, activities of components may be quite different from concentrations. The activity coefficient is, therefore, a very important parameter that we will use frequently to deal with nonideal thermodynamic behavior. Activity coefficients should be obtained from experimental observations, though they can sometimes also be predicted from molecular theory (such as the Debye–Hückel theory for dilute electrolyte solutions, to be discussed in Chapter 6).

An example may be helpful to appreciate the implications. Figure 3.12 shows the nonideal behavior of sucrose–water solutions, both for the solute sucrose (Figure 3.12A) and the solvent water (Figure 3.12B),

TABLE 3.8 Overview of Possible Standard States and the Symbols Used

System	Standard State	Symbol	Activity	Chemical Potential
Perfect gas	Gas having partial pressure of 1 bar	°	$a_i = \frac{P_i}{1\text{bar}}$	$\mu_i = \mu_i^\circ + RT \ln \frac{P_i}{P^\circ}$
Real gas	Gas having partial pressure of 1 bar extrapolated from the behavior of $P \rightarrow 0$	°	$a_i = f_i P_i$ $\lim_{P_i \rightarrow 0} \left(\frac{a_i}{P_i} \right) = 1$	$\mu_i = \mu_i^\circ + RT \ln \frac{f_i P_i}{P^\circ}$
Solid	Pure solid at $P = 1$ bar	*	$a_i = 1$	$\mu_i = \mu_i^* = \mu_i^\circ$
Liquid	Pure liquid at $P = 1$ bar	*	$a_i = 1$	$\mu_i = \mu_i^* = \mu_i^\circ$
Ideal solution	Pure liquid at $X = 1$	*	$a_i = X_i$	$\mu_i = \mu_i^* + RT \ln X_i$
Solvent in real solution	Pure solvent at $X_s = 1$	*	$a_i = f_i X_s$ $\lim_{X_s \rightarrow 1} \left(\frac{a_s}{X_s} \right) = 1$	$\mu_s = \mu_s^* + RT \ln f_s X_s$
Solute in real solution	$X_i = 1$, extrapolated from infinite dilution	⊖	$a_i = f_i X_i$ $\lim_{X_i \rightarrow 0} a_i = X_i$	$\mu_i = \mu_i^\ominus + RT \ln f_i X_i$
	$m = 1 \text{ mol kg}^{-1}$ solvent		$a_i = \gamma_i m_i$ $\lim_{m_i \rightarrow 0} a_i = m_i$	$\mu_i = \mu_i^\ominus + RT \ln \frac{\gamma_i m_i}{m^\ominus}$
	$c = 1 \text{ mol L}^{-1}$ solution, extrapolated from infinite dilution		$a_i = \gamma_i c_i$ $\lim_{c_i \rightarrow 0} a_i = c_i$	$\mu_i = \mu_i^\ominus + RT \ln \frac{\gamma_i c_i}{c^\ominus}$
Solute in real solution in biochemist's standard state	Solute at $m = 1 \text{ mol kg}^{-1}$ solvent, or $c = 1 \text{ mol L}^{-1}$ solution at pH 7	⊖'	$a_{\text{H}^+} = 1$ at pH 7 Activities of other species = total concentration of all species of that molecule at pH 7.0	$\mu'_i = \mu_i^{\ominus'} + RT \ln \frac{a_i}{a^\ominus}$

Note: $P^\circ = 1 \text{ bar}$, $a^\ominus = 1 \text{ mol L}^{-1}$ solution or 1 mol kg^{-1} solvent.

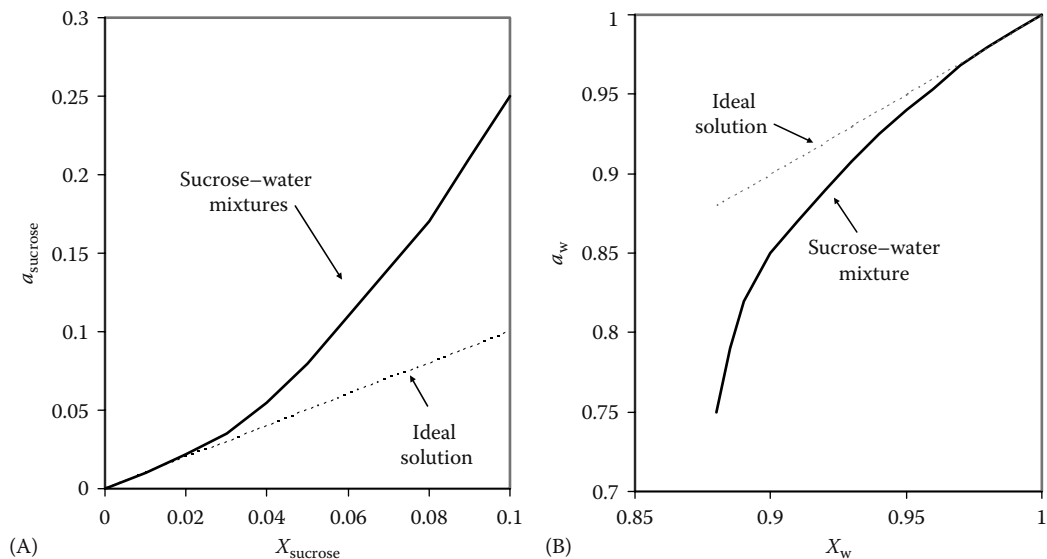


FIGURE 3.12 Example of nonideal behavior of sucrose–water solutions. Activity of sucrose as a function of the mole fraction of sucrose (A) and the activity of water as a function of the mole fraction of water (B). Data set in Appendix 3.1, Table A.3.3.

TABLE 3.9 Relation between the Various Activity Coefficients of Sucrose, f , γ , γ , for Three Aqueous Sucrose Solutions

% Sucrose Solution (w/w)	ρ_{sln} (g cm ⁻³)	a_{sucrose} (Based on Mole Fraction X)	X_{sucrose}	f	m_{sucrose} (mol kg ⁻¹ water)	γ	c_{sucrose} (mol dm ⁻³ solution)	γ
10.3	1.0393	0.006	0.006	1.0	0.335	0.994	0.31	1.11
39.7	1.1750	0.0481	0.0335	1.44	1.93	1.38	1.36	2.30
69.9	1.3465	0.3045	0.1089	2.80	6.79	2.49	2.75	8.28

Note: $M_{\text{sucrose}} = 342$, $M_{\text{water}} = 18$.

expressed on the basis of mole fractions. Since sucrose solutions behave as nonideal solutions, the activity coefficients deviate from unity except in very dilute solution. Table 3.9 displays three concentrations for sucrose in aqueous solution. The values of the various activity coefficients are seen to differ substantially, depending on what basis they are expressed. Consequently, also the activities are different depending on the standard state used. Activities based on mole fractions are always between 0 and 1, but activities based on molarity and molality can have any positive value.

Activities of ionic solutes are even more complicated because electrolytes in aqueous solutions dissociate and, moreover, depend on ionic strength and valencies. Ionic compounds occur abundantly in foods, and the activity concept is very relevant. In view of its importance, this is discussed in more detail in Chapter 6.

Gibbs–Duhem relation. The chemical potentials of components in mixtures are not completely independent. The following relation holds for the change in free energy:

$$dG = -SdT + PdV + \sum_i n_i d\mu_i \quad (3.67)$$

At equilibrium $dG = 0$, and we have the Gibbs–Duhem relation

$$-SdT + VdP + \sum_i n_i d\mu_i = 0 \quad (3.68)$$

At constant temperature and pressure this reduces to

$$\sum_i n_i d\mu_i = 0 \quad (3.69)$$

For a two-component system, for instance, this results in

$$\frac{d\mu_1}{d\mu_2} = \frac{X_2}{1 - X_2} \quad (3.70)$$

In other words, if we know the chemical potential of one of two components in a binary mixture, we can calculate the other one by numerical or graphical integration. Some more information can be found in Appendix C.

3.3.11 Solvent Activity and Water Activity

The activity of the solvent has been discussed above in general terms. In foods, water is usually the solvent of interest. Figure 3.12B shows water activity in aqueous sucrose solutions. Water activity is used

as an important parameter in food stability, although this may not be warranted always, because water activity is a thermodynamic parameter whereas stability is about kinetics. In foods, water is not only a solvent but also often a reactant (e.g., in hydrolysis reactions), which makes the situation more complicated. This is discussed further in Chapter 14, building on the general outline given here.

To recapitulate, the chemical potential of water as a solvent (in terms of mole fraction, see Table 3.8) for an ideal solution is expressed as

$$\mu_w = \mu_w^o + RT \ln X_w \quad (3.71)$$

In the case that we deal with binary mixtures it is most convenient to work with concentrations on the mole fraction scale. However, in the case of solutions, when usually the number of moles of solute is much less than the number of moles of solvent, it is much more convenient to work with molalities (or molarities) for the solute, and the reference state for solute i is then an aqueous solution, not pure i . However, for the solvent the mole fraction remains the most convenient scale. The relation between water mole fraction X_w and molality m_i of solute i is

$$X_w = \frac{1}{1 + m_i M_w} \quad (3.72)$$

M_w is the molar mass of water ($0.018 \text{ kg mol}^{-1}$). The relation between water activity in an ideal solution a_w^{id} and solute molality m_i is then

$$\ln a_w^{\text{id}} = \ln X_w = \ln \left(\frac{1}{1 + m_i M_w} \right) = -\ln (1 + m_i M_w) = -M_w m_i \quad (3.73)$$

In the last equation, use is made of the expansion

$$\ln (1 + x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 - \frac{1}{4}x^4 + \dots \quad (3.74)$$

neglecting the higher order terms. So, Equation 3.73 shows how water activity depends on a solute in the case of an ideal solution: only the molality of the solute counts, not its nature. (For salts, Equation 3.73 needs to be modified to account for dissociation into ions; we come back to this in Chapter 6.)

Now we move to nonideal solutions and therefore we have to work with activities. Water activity cannot be predicted theoretically from the composition of a solution. Many empirical relations have been published to predict water activity from composition but we will not discuss these here and refer to some selected references at the end of this chapter and Chapter 14. The water activity of a solution always decreases when a solute is added because of the mere fact that the mole fraction of water decreases. This means that the water is stabilized in the sense that the Gibbs energy is decreased with respect to pure water. The question remains how much the water activity is decreased upon addition of a solute. The chemical potential of water in an aqueous solution with one or more solutes is expressed on the mole fraction scale as

$$\mu_w = \mu_w^o + RT \ln a_w = \mu_w^o + RT \ln f_w X_w = \mu_w^o + RT \ln X_w + RT \ln f_w \quad (3.75)$$

In this equation f_w represents the rational activity coefficient of water. The part $RT \ln f_w$ is called the excess chemical potential* since it describes the deviation of ideal behavior

$$\mu_w^E = RT \ln f_w \quad (3.76)$$

* An excess function is defined as the difference between the value of a function for a real system and that of an ideal system.

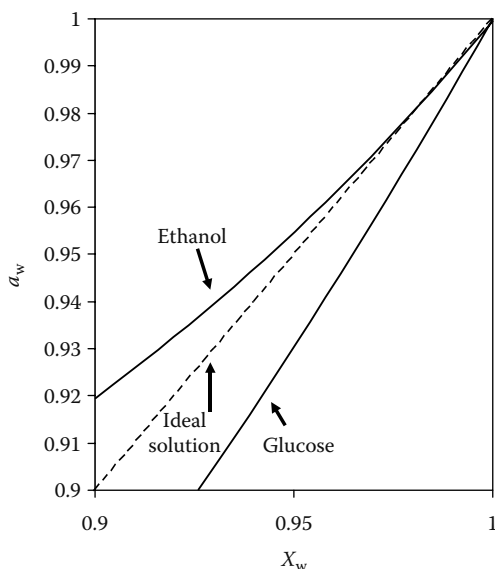


FIGURE 3.13 Water activity as a function of water mole fraction, which is varied by addition of ethanol or glucose. Data set in Appendix 3.1, Table A.3.4.

The activity coefficient f_w can be larger or smaller than unity (but is always positive). If $f_w < 1$ then the solute stabilizes the water more than in the ideal case (negative excess chemical potential), and if $f_w > 1$ then the water is less stabilized than in the ideal case (positive excess chemical potential). Figure 3.13 gives two examples. A solution of ethanol causes a positive excess chemical potential of water, while a glucose solution cause the excess chemical potential to be negative.

Figure 3.13 shows that at the same water mole fraction, water activity can be quite different, depending on which solute is present. Activities can be estimated experimentally from osmotic measurements, electromotive force measurements, ion selective electrodes, and the like. We are interested in how solutes affect water activity but nonideal behavior is not immediately apparent from water activity values. There is another way to see whether there is nonideal behavior, via the so-called osmotic coefficient. The osmotic coefficient provides a more sensitive measure of the deviation of the solvent from ideal behavior than the rational activity coefficient f_w . Osmotic coefficient and activity coefficient both describe the deviation from nonideal behavior of the solvent in a real mixture. The activity coefficient on the mole fraction scale is according to Equation 3.75

$$\mu_w = \mu_w^0 + RT \ln f_w X_w \left(\lim_{X_w \rightarrow 1} f_w = 1 \right)$$

In the case of mole fractions, we can also use the rational osmotic coefficient g_o

$$\mu_w = \mu_w^0 + g_o RT \ln X_w \left(\lim_{X_w \rightarrow 1} g_o = 1 \right) \quad (3.77)$$

and in the case of molalities the practical osmotic coefficient Φ

$$\mu_w = \mu_w^0 - \Phi RT M_w m_i \left(\lim_{m_i \rightarrow 0} \Phi = 1 \right) \quad (3.78)$$

The relation between Φ and g_o is

$$\begin{aligned}\Phi &= -\frac{\ln X_w}{M_w m_i} g_o \\ &= \left[1 + \frac{M_w m_i}{2} + \frac{(M_w m_i)^2}{3} + \dots \right] g_o \quad (3.79)\end{aligned}$$

Figure 3.14 gives an example for sucrose to illustrate that the osmotic coefficient is much more sensitive to nonideal behavior than water activity itself.

The relation between water activity and practical osmotic coefficient Φ is

$$\ln a_w = -\Phi M_w m_i \quad (3.80)$$

Comparison with Equation 3.73 shows that for ideal solutions $\Phi = 1$. The practical osmotic coefficient is tabulated for many solutes in aqueous solutions. Via the Gibbs–Duhem relation a relation can be found between the practical osmotic coefficient of a solution and the activity coefficient of a solute i in that solution

$$(\Phi - 1) \frac{dm_i}{m_i} + d\Phi = d \ln \gamma_i \quad (3.81)$$

This can be rearranged into

$$\ln \gamma_i = \Phi - 1 + \int_0^{m_i} \frac{\Phi - 1}{m_i} dm_i \quad (3.82)$$

The excess chemical potential of water expressed in terms of the practical osmotic coefficient is

$$\mu_w^E = (1 - \Phi)RTM_w m_i \quad (3.83)$$

Several theories have been put forward to explain the effects of nonideal behavior of solutes. One of them relates to hydration of solute molecules, implying that water molecules are actually taken away from the bulk water, resulting in a lower water activity. Another way of looking at this is called molecular recognition: when two solutes in an aqueous solution signal their presence to each other via their effect on water molecules. This pairwise interaction involves a potential of average force between the solutes. Pairwise interactions come from a virial expansion of pair and higher order coefficients, accounting for all variations of solute–solute and solute–solvent interactions. The so-called Savage–Wood additivity of group interactions (SWAG) allows for a quantitative account. For simple, nonionic compounds the deviation from ideality can be quantified in the pairwise Gibbs energy interaction parameter g_{ii} (J kg^{-1})

$$1 - \Phi = -\frac{1}{RT} g_{ii} \frac{m_i}{(m^0)^2} \quad (3.84)$$

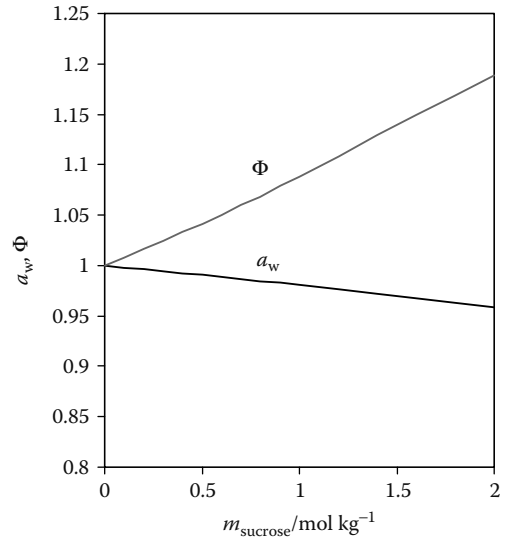


FIGURE 3.14 Practical osmotic coefficient Φ and water activity a_w as a function of the molality of sucrose solutions. Data set in Appendix 3.1, Table A.3.5.

m^0 is the standard molality of 1 mol kg⁻¹. Combining Equations 3.80 and 3.84 results in

$$\ln a_w = -M_w m_i \left[1 + \frac{1}{RT} g_{ii} \frac{m_i}{(m^0)^2} \right] \quad (3.85)$$

This equation can also be written as

$$\ln a_w + M_w m_i = -M_w \frac{1}{RT} g_{ii} \frac{m_i^2}{(m^0)^2} \quad (3.86)$$

Thus, Equation 3.86 shows that g_{ii} can be estimated from a plot of $(\ln a_w + M_w m_i)$ versus m_i^2 . If g_{ii} turns out to be positive this can be interpreted as repulsion between solute molecules, while a negative g_{ii} leads to the conclusion that there is attraction between solute molecules. Of course, $g_{ii} = 0$ corresponds to an ideal solution and then Equation 3.86 reduces to Equation 3.73.

It should be realized that the concept of water activity is a thermodynamic one and therefore relates to equilibrium conditions. Foods are often not in an equilibrium state, as argued before, and therefore the concept of water activity for foods is a bit tricky. It would be better to use relative vapor pressures because that is what is measured (as indicated in Equation 3.57). However, this may be more a theoretical argument than a practical one. In practice, water activities are used frequently and one just assumes that the water activity is equal to the relative vapor pressure, as expressed in Equation 3.57. Water activity can differ, sometimes strongly, between the inner and outer part of a food. Differences in chemical potential are a driving force for transport, as we will see later on, and so, when this happens, there will be water migration unless it is prevented by some barrier.

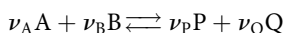
Now that we have discussed the meaning of chemical potentials and activities, we can return to chemical potentials in relation to chemical reactions where activities play a central role.

3.3.12 Chemical Potential and Equilibrium

As discussed above, the Gibbs energy change is a measure for the direction of processes, in other words, it indicates the ability to react. As a reminder if a chemical reaction occurs in a system, it will proceed in such a way that it decreases the free energy. Let us take a closer look at how chemical reactions are related to free energy changes. If we consider both reactants and products at standard conditions, the standard free energy change is simply the difference between the free energy of the sum of the products and that of the reactants

$$\Delta G^\ominus = \sum G_{\text{products}}^\ominus - \sum G_{\text{reactants}}^\ominus \quad (3.87)$$

The free energy G of a mixture depends on the number of moles n_i of each component and their chemical potentials μ_i at that particular composition (cf. Equation 3.42). Suppose we have a chemical reaction as depicted in Equation 3.1:



The value of the Gibbs energy of the mixture of reactants A, B, consisting of moles n_A and n_B , and products P, Q in moles n_P and n_Q , is then

$$G = n_A \mu_A + n_B \mu_B + n_P \mu_P + n_Q \mu_Q \quad (3.88)$$

Now, we consider free energy as a function of composition as the reaction proceeds from left to right in Equation 3.1. Using the concept of degree of reaction α_r (Equation 3.10; the same result would be obtained when using the extent of reaction ξ but ξ can have a value > 1 , whereas $0 < \alpha_r < 1$, which is more convenient for the present discussion), the reaction Gibbs energy under standard conditions can be expressed as

$$G_r^\ominus = (1 - \alpha_r)(G_A^\ominus + G_B^\ominus) + \alpha_r(G_P^\ominus + G_Q^\ominus) = G_A^\ominus + G_B^\ominus + \alpha_r(G_P^\ominus + G_Q^\ominus - (G_A^\ominus + G_B^\ominus)) \quad (3.89)$$

This can be rewritten as

$$G_r^\ominus = G_A^\ominus + G_B^\ominus + \alpha_r \Delta_r G^\ominus \quad (3.90)$$

So, when $G_r^\ominus$ is plotted as a function of α_r , a straight line with slope $\Delta_r G^\ominus$ is obtained (Figure 3.15).

Of course, it is a hypothetical situation for reactants and products to remain both in their standard state during the reaction. Reactants and products mix due to the very reaction: at first there are only reactants but products start to be formed as the reaction progresses. Therefore, reactants and products cannot remain in the standard state. So, we have to study what will happen under nonstandard conditions. An extra contribution to the free energy comes from the mixing effect so that Equation 3.90 becomes

$$G = G_A^\ominus + G_B^\ominus + \alpha_r \Delta_r G^\ominus + \Delta_{\text{mix}} G \quad (3.91)$$

As discussed above, for a real mixture the relation holds

$$\mu_i = \mu_i^* + RT \ln f_i X_i \quad (3.92)$$

and for the mixing term

$$\Delta_{\text{mix}} G = \sum X_i (\mu_i - \mu_i^*) = \sum X_i RT \ln X_i + \sum X_i RT \ln f_i \quad (3.93)$$

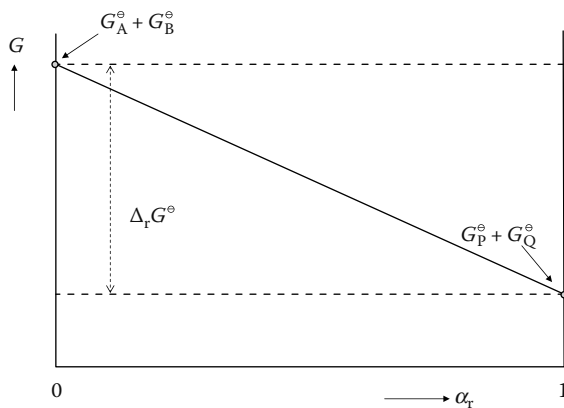


FIGURE 3.15 Free energy of a reaction is depicted as a function of the degree of reaction α_r with both reactants and products in the standard state. A, B represent reactants, P, Q represent products.

As before, the deviation from ideality is accounted for in the activity coefficient. The first term in the right-hand side of Equation 3.93 reflects ideal mixing and is always negative while the second term reflects nonideal mixing. This second term is called the excess Gibbs energy of mixing. Recall that we are looking for an equation that expresses how G changes with α_r . For ideal solutions, there is no volume change when the composition changes and $\Delta_{\text{mix}}H = 0$, so in that case the extra contribution in $\Delta_{\text{mix}}G$ is due to entropy effects, as was shown already in Equations 3.40. Equation 3.40 shows that ΔS contains both a concentration-independent term and a concentration-dependent term; see also Equation 3.52. The concentration-dependent term is called the entropy of mixing. It reflects the change in number of accessible microstates upon mixing of two or more chemical species. It is the dispersal of energy of each species within a larger volume due to mixing that affects entropy. Hence, the entropy of mixing is the difference between the entropy of the mixed state and the entropy of the corresponding unmixed state. Expressed in mole fractions X_i the expression for a reaction as depicted in Equation 3.1 taking place in an ideal solution would be (cf. Equation 3.52)

$$\Delta_{\text{mix}}S = -NR(X_A \ln X_A + X_B \ln X_B + X_P \ln X_P + X_Q \ln X_Q) = -NR \sum_i X_i \ln X_i \quad (3.94)$$

N is the total number of moles in the system, and R is the gas constant, as usual. When a reaction starts with reactants A and B, the reaction mixture becomes more mixed when products are formed, and consequently, the entropy of mixing increases. When the reaction would go to completion, i.e., no reactants left anymore, some demixing occurs, leading to a decrease in mixing entropy.

The change in entropy of mixing with α_r can be derived from Equation 3.94 and when activities are used instead of mole fractions it results in

$$\frac{d(\Delta_{\text{mix}}S)}{d\alpha_r} = -R \ln \left(\frac{a_P^{\nu_P} a_Q^{\nu_Q}}{a_A^{\nu_A} a_B^{\nu_B}} \right) \quad (3.95)$$

$\Delta_{\text{mix}}S = 0$ in the unmixed state and ≥ 0 when the reaction progresses. It reaches its maximum value when reactants and products become maximally mixed. Using the relation $\Delta G = \Delta H - T\Delta S$, and remembering that $\Delta_{\text{mix}}H = 0$ for an ideal solution, it follows that

$$\frac{d(\Delta_{\text{mix}}G)}{d\alpha_r} = -\frac{d(T\Delta S)}{d\alpha_r} = RT \ln \left(\frac{a_P^{\nu_P} a_Q^{\nu_Q}}{a_A^{\nu_A} a_B^{\nu_B}} \right) = RT \ln Q_r \quad (3.96)$$

Thus, the reaction quotient Q_r is defined as

$$Q_r = \frac{a_P^{\nu_P} a_Q^{\nu_Q}}{a_A^{\nu_A} a_B^{\nu_B}} \quad (3.97)$$

The expression of how G changes with α_r can now be found by evaluating Equation 3.90 with respect to α_r and substituting Equations 3.96 and 3.97

$$\frac{dG}{d\alpha_r} = \frac{d(\alpha_r \Delta_r G^\ominus)}{d\alpha_r} + \frac{d(\Delta_{\text{mix}}G)}{d\alpha_r} = \Delta_r G^\ominus + RT \ln Q_r \quad (3.98)$$

This equation shows the contribution of the entropy of mixing to the change in free energy but now expressed as $RT \ln Q_r$. One can thus calculate the change in free energy as a function of the extent of reaction

$$G_{\alpha_r} - G_{\alpha_r=0} = \alpha_r \Delta_r G^\ominus + RT \ln Q_r \quad (3.99)$$

If $dG/d\alpha_r < 0$ the reaction will proceed from left to right because that is the direction of free energy decrease, and if $dG/d\alpha_r > 0$ for such a reaction it will move in the opposite direction from right to left, again because that decreases free energy. Equilibrium is attained when $dG/d\alpha_r = 0$ and then the reaction quotient Q_r has become equal to the equilibrium constant K_{eq}

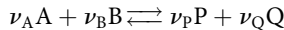
$$K_{eq} = \frac{a_P^{\nu_P} a_Q^{\nu_Q}}{a_A^{\nu_A} a_B^{\nu_B}} \quad (3.100)$$

Another expression that describes equilibrium is

$$\sum \nu_i \mu_i = 0 \quad (3.101)$$

3.3.13 Equilibrium Constants

Recalling Equation 3.1



Equations 3.97 and 3.100 are an expression of the famous law of mass action; we will come back to this when discussing chemical kinetics in Chapter 4. Equation 3.100 shows how *activities* are related to each other when equilibrium is attained. Note that K_{eq} is dimensionless because activities are dimensionless. This is called a thermodynamic equilibrium constant and it is this constant that is reported in tables. In practice, however, it may be more convenient to use constants based on pressures, concentrations, or molalities but it should be realized that these are actually not true constants (except at very low concentrations) because they depend on activity coefficients, and these vary with composition. The following analysis shows how practical equilibrium constants are related to the true thermodynamic equilibrium constant. It is easiest to start with considering the reaction in Equation 3.1 in the gas phase, and consider it as an ideal mixture of perfect gases so that we can use pressures instead of fugacities, and Equation 3.100 can be written as

$$K_{eq} = \frac{\left(\frac{P_P}{P^\ominus}\right)^{\nu_P} \left(\frac{P_Q}{P^\ominus}\right)^{\nu_Q}}{\left(\frac{P_A}{P^\ominus}\right)^{\nu_A} \left(\frac{P_B}{P^\ominus}\right)^{\nu_B}} = \frac{(P_P)^{\nu_P} (P_Q)^{\nu_Q}}{(P_A)^{\nu_A} (P_B)^{\nu_B}} \left(\frac{1}{P^\ominus}\right)^{\nu_P + \nu_Q - \nu_A - \nu_B} = K_P \left(\frac{1}{P^\ominus}\right)^{\Delta\nu} \quad (3.102)$$

K_P is the equilibrium constant in terms of pressure. Since $P^\ominus = 1$ bar, this equation shows that $K_{eq} = K_P$, as it should be, because we have assumed an ideal gas. To change from pressures to concentrations, we can use the ideal gas law that reads

$$P = \frac{N}{V} RT \quad (3.103)$$

The concentration is in fact N/V so that Equation 3.100 changes to

$$K_{eq} = \frac{[P]^{\nu_P} [Q]^{\nu_Q}}{[A]^{\nu_A} [B]^{\nu_B}} \left(\frac{RT}{P^\ominus}\right)^{\Delta\nu} = K_c \left(\frac{RT}{P^\ominus}\right)^{\Delta\nu} \quad (3.104)$$

This shows that the equilibrium constant in terms of concentration (with a hypothetical standard state of 1 mol dm^{-3}) is different from K_{eq} unless $\Delta\nu = 0$. The relation between K_c and K_p follows from Equations 3.102 and 3.104

$$K_c = K_p(RT)^{-\Delta\nu} \quad (3.105)$$

Similarly, the relation between K_X , the equilibrium constant in terms of mole fraction and K_p is

$$K_X = K_p P^{-\Delta\nu} \quad (3.106)$$

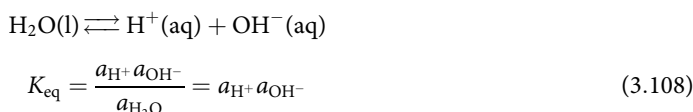
(P is the total pressure). Unless $\Delta\nu = 0$, these equations show that the mole fractions or the concentrations in an equilibrium mixture will depend on the pressure P , even though K_p does not.

As mentioned, thermodynamic equilibrium constants are tabulated for activities, not for concentrations. The expression for K_{eq} as in Equation 3.100 based on activities is universally valid and K_{eq} is a true constant (though depending on temperature) but the difficulty is of course in relating activities to measurable quantities. To convert activities to concentrations we need activity coefficients, and as we have seen these depend on the choice of standard state. Practical equilibrium constants such as K_c depend on concentration because activity coefficients depend on concentration. This becomes clear from the following analysis:

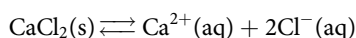
$$K_{\text{eq}} = \frac{a_p^{\nu_p} a_Q^{\nu_Q}}{a_A^{\nu_A} a_B^{\nu_B}} = \frac{[P]^{\nu_p} [Q]^{\nu_Q}}{[A]^{\nu_A} [B]^{\nu_B}} \frac{\gamma_p^{\nu_p} \gamma_Q^{\nu_Q}}{\gamma_A^{\nu_A} \gamma_B^{\nu_B}} = K_c \frac{\gamma_p^{\nu_p} \gamma_Q^{\nu_Q}}{\gamma_A^{\nu_A} \gamma_B^{\nu_B}} \quad (3.107)$$

Activity coefficients depend on concentration which implies that K_c must also depend on concentration to keep K_{eq} constant. The same is of course true for K_m based on molalities. So, K_m and K_c are not really true equilibrium constants unless the activity coefficients are equal to one; such a situation may occur in (very) diluted solutions.

The standard states need not be the same for all components that are involved in the reaction. However, it is essential that the same standard state is used for the standard chemical potential and for the activity coefficient because these two determine the chemical potential (as is shown in several equations above, e.g., in Table 3.8). The reader is reminded that activities in Equation 3.100 are by definition equal to 1.0 for pure solids and pure liquids while for gases it is equal to pressure (at a standard pressure $P^\circ = 1 \text{ bar}$). Since the activities of pure liquids and solids hardly depend on pressure, we do not need to include activities of pure liquids and solids in calculation of equilibria because they are approximately equal to 1.0 at moderate pressures. For instance, the equilibrium constant for dissociation of water



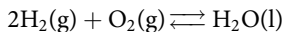
with $a_{\text{H}_2\text{O}} = 1$ and this constant is commonly called the water dissociation constant K_w . For the dissolution of a salt in water, assuming a saturated solution



the equilibrium constant is

$$K_{\text{eq}} = \frac{a_{\text{Ca}^{2+}} a_{\text{Cl}^-}^2}{a_{\text{CaCl}_2}} = a_{\text{Ca}^{2+}} a_{\text{Cl}^-}^2 \quad (3.109)$$

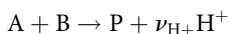
The latter equilibrium constant is usually referred to as the solubility product. For the formation of water from oxygen and hydrogen:



The equilibrium constant is

$$K_{\text{eq}} = \frac{a_{\text{H}_2\text{O}}}{P_{\text{H}_2}^2 P_{\text{O}_2}} = \frac{1}{P_{\text{H}_2}^2 P_{\text{O}_2}} \quad (3.110)$$

Perhaps it is useful to come back here briefly to the biochemists' standard state. To recall, the hydrogen ion concentration for the standard state is defined as 10^{-7} M, and as a result the change in standard Gibbs free energy will be different for reactions in which H^+ ions are produced or consumed. So, if we have a reaction:



Equation 3.98 becomes

$$\frac{dG}{d\alpha_r} = \Delta_r G^{\ominus'} + RT \ln \frac{\frac{[\text{P}]}{c^{\ominus}} \left(\frac{[\text{H}^+]}{10^{-7} \text{M}} \right)^{\nu_{\text{H}^+}}}{\frac{[\text{A}][\text{B}]}{c^{\ominus} c^{\ominus}}} \quad (3.111)$$

Comparing this with the “normal” standard state of $c^{\ominus} = 1 \text{ mol dm}^{-3}$, it follows that

$$\Delta_r G^{\ominus} = \Delta_r G^{\ominus'} + \nu_{\text{H}^+} RT \ln \frac{1}{10^{-7}} \quad (3.112)$$

If, for instance, $\nu_{\text{H}^+} = 1$, the difference between $\Delta_r G^{\ominus}$ and $\Delta_r G^{\ominus'}$ is 40 kJ mol^{-1} . Similarly, if H^+ ions are taken up in the reaction, the difference is $-40.0 \text{ kJ mol}^{-1}$ for $\nu_{\text{H}^+} = 1$. For reactions in which no H^+ is involved, there is no difference in standard free energies.

Equilibrium constants and free energy changes. When equilibrium is attained so that $dG/d\alpha_r = 0$ and $Q_r = K_{\text{eq}}$, it follows from Equation 3.98, that the equilibrium constant of a reaction is linked to the standard Gibbs energy change

$$\Delta_r G^{\ominus} = -RT \ln K_{\text{eq}} \quad (3.113)$$

This is a very important relationship because it shows that equilibrium constants can be predicted from standard Gibbs energy changes, which are tabulated for many reactions, or can be calculated from standard Gibbs energies of formation (by analogy of Equation 3.20). Table 3.10 shows some numerical examples and gives a feel what the values imply for the relative amount of reactants and products.

Incidentally, the fact that $\Delta_r G^{\ominus}$ appears in Equation 3.113 is due to the relation between the chemical potential and molar Gibbs energy (Equation 3.42). In the case of constant temperature and volume, we should use the Helmholtz energy F , but $\Delta_r G^{\ominus}$ then still appears in the equations. For instance, Equation 3.98 in the case of constant T , V becomes

$$\frac{dF}{d\alpha_r} = \Delta_r G^{\ominus} + RT \ln Q_r \quad (3.114)$$