

Thermodynamics of Natural Systems

Theory and Applications in Geochemistry and Environmental Science

Third Edition

Thermodynamics deals with energy levels and energy transfers between states of matter, and is therefore fundamental to all branches of science. This new edition provides an accessible introduction to the subject, specifically tailored to the interests of Earth and environmental science students. Beginning at an elementary level, the first four chapters explain all necessary concepts via a simple graphical approach. Throughout the rest of the book the author emphasizes the importance of field observations and demonstrates that, despite being derived from idealized circumstances, thermodynamics is crucial to understanding ore formation, acid mine drainage, and other real-world geochemical and geophysical problems. Exercises now follow each chapter, with answers provided at the end of the book. An associated website includes extra chapters and password-protected answers to additional problems. This textbook is ideal for undergraduate and graduate students studying geochemistry and environmental science.

Greg Anderson is Professor Emeritus in the Department of Earth Sciences at the University of Toronto. He began his career as a mining engineer and exploration geologist before becoming interested in geochemistry. After completing his Ph.D. at Toronto he spent five years at Pennsylvania State University doing experimental work on mineral solubilities. Afterward, he returned to Toronto, where he has since divided his time between studies of mineral systems, lead-zinc ore deposits, and theoretical geochemistry. He is the co-author of two other textbooks for Earth scientists, and in 2000 was awarded the Past Presidents' Medal (now named the Peacock Medal) by the Mineralogical Association of Canada for contributions to geochemistry.

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and Environmental Science

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G.M. ANDERSON



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To my wife, Khodjasteh Hedjran Anderson

CONTENTS

Preface	<i>page</i> xiii
Online Resources and Exercises	xvii
1 What Is Thermodynamics?	
1.1 Introduction	1
1.2 What Is the Problem?	1
1.3 A Mechanical Analogy	2
1.4 Thermodynamic Potentials	5
1.5 Idealization in Thermodynamics	7
1.6 Limitations of the Thermodynamic Model	8
1.7 Summary	9
Exercises	9
Additional Problems	10
2 Defining Our Terms	
2.1 Something Is Missing	11
2.2 Systems	11
2.3 Equilibrium	15
2.4 State Variables	20
2.5 Phases, Components, and Species	22
2.6 Processes	23
2.7 Notation	31
2.8 Time as a Thermodynamic Variable	33
2.9 Thermodynamics and Natural Systems	34
2.10 Summary	35
Exercises	36
Additional Problems	37
3 The First Law of Thermodynamics	
3.1 Temperature and Pressure Scales	38
3.2 Internal Energy	39
3.3 Energy Transfers	42
3.4 The First Law of Thermodynamics	44
3.5 Work	45
3.6 Heat	55
3.7 How Far Have We Got?	61
3.8 The Model Again	61

Contents

3.9	Summary	63
	Exercises	64
	Additional Problems	65
4	The Second Law of Thermodynamics	
4.1	Introduction	66
4.2	The Problem Restated	66
4.3	Thermodynamic Potentials	68
4.4	Entropy	70
4.5	The Fundamental Equation	74
4.6	The U – S – V Surface	75
4.7	Applicability of the Fundamental Equation	77
4.8	Constraints and Metastable States	78
4.9	The Energy Inequality Expression	81
4.10	Entropy and Heat Capacity	84
4.11	A More Useful Thermodynamic Potential	90
4.12	Gibbs and Helmholtz Functions as Work	95
4.13	Open Systems	98
4.14	The Meaning of Entropy	101
4.15	The End of the Road	104
4.16	Summary	104
	Exercises	106
	Additional Problems	107
5	Getting Data	
5.1	Introduction	110
5.2	What to Measure?	111
5.3	Solution Calorimetry	113
5.4	The Third Law	118
5.5	The Problem Resolved	121
5.6	Data at Higher Temperatures	127
5.7	Data at Higher Pressures	131
5.8	Summary	132
	Exercises	133
	Additional Problems	134
6	Some Simple Applications	
6.1	Introduction	137
6.2	Simple Phase Diagrams	137
6.3	The Slope of Phase Boundaries	141
6.4	Another Example	144
6.5	Summary	148
	Exercises	148
	Additional Problems	149

Contents

7	Solutions	
	7.1 Introduction	150
	7.2 Measures of Concentration	150
	7.3 Properties of Ideal Solutions	153
	7.4 Ideal Solution Laws	155
	7.5 Ideal Solution Equations	160
	7.6 Real Solutions	167
	7.7 Solution Volumes	168
	7.8 Next Step – The Activity	173
	7.9 Summary	173
	Exercises	174
	Additional Problems	175
8	Fugacity and Activity	
	8.1 Fugacity	177
	8.2 Activity	180
	8.3 Standard States and Activity Coefficients	184
	8.4 Activities and Standard States: An Overall View	187
	8.5 Summary	190
	Exercises	191
	Additional Problems	192
9	The Equilibrium Constant	
	9.1 Reactions in Solution	195
	9.2 Reactions at Equilibrium	196
	9.3 The Most Useful Equation in Thermodynamics	198
	9.4 Special Meanings for K	203
	9.5 K in Solid–Solid Reactions	207
	9.6 Change of K with Temperature I	210
	9.7 The Amino Acid Example Again	215
	9.8 Some Conventions Regarding Components	218
	9.9 Summary	222
	Exercises	222
	Additional Problems	226
10	Rock–Water Systems	
	10.1 Real Problems	231
	10.2 Is the Sea Saturated with Calcium Carbonate?	231
	10.3 Determining the IAP – Speciation	234
	10.4 Combining the IAP and the K_{sp}	241
	10.5 Mineral Stability Diagrams	243
	10.6 Summary	249
	Exercises	250
	Additional Problems	251

Contents

11 Redox Reactions	
11.1 Introduction	257
11.2 Electron Transfer Reactions	257
11.3 The Role of Oxygen	258
11.4 A Simple Electrolytic Cell	259
11.5 The Nernst Equation	263
11.6 Some Necessary Conventions	265
11.7 Measuring Activities	268
11.8 Measuring Redox Conditions	270
11.9 <i>Eh</i> –pH Diagrams	274
11.10 Oxygen Fugacity	278
11.11 Summary	281
Exercises	283
Additional Problems	287
12 Phase Diagrams	
12.1 What Is a Phase Diagram?	293
12.2 The Phase Rule	294
12.3 Unary Systems	296
12.4 Binary Systems	303
12.5 Ternary Systems	327
12.6 Summary	336
Exercises	336
Additional Problems	340
13 Affinity and Extent of Reaction	
13.1 Introduction	343
13.2 Quasistatic Processes	343
13.3 The Extent of Reaction Variable	344
13.4 Components and Species Again	348
13.5 The Affinity	349
13.6 Conclusion	355
13.7 Final Comment	355
Exercises	357
Additional Problems	357
APPENDICES	
Appendix A Constants and Numerical Values	359
Appendix B Standard State Thermodynamic Properties of Selected Minerals and Other Compounds	361
Appendix C Answers to Exercises	375
References	403
Index	408

ONLINE MATERIALS: ADDITIONAL CHAPTERS FROM THE SECOND EDITION

Available at www.cambridge.org/thermodynamics

10	Real Solutions	
10.1	Introduction	1
10.2	Solution Volumes	1
10.3	The Infinite Dilution Standard State	12
10.4	Excess Properties	13
10.5	Enthalpy and Heat Capacity	20
10.6	Gibbs Energies	28
10.7	Margules Equations	35
10.8	Beyond Margules	39
10.9	The Gibbs–Duhem Equation	39
10.10	Summary	41
11	The Phase Rule	
11.1	Introduction	42
11.2	Derivation of the Phase Rule	42
11.3	Components and Species	45
11.4	Duhem’s Theorem	50
11.5	Buffered Systems	53
11.6	Summary	57
13	Equations of State	
13.1	Introduction	58
13.2	The Ideal Gas	58
13.3	Two Kinds of EoS	63
13.4	Cubic Equations of State	63
13.5	The Virial Equation	69
13.6	Thermal Equations of State	74
13.7	Other Equations of State	81
13.8	Summary	83
14	Solid Solutions	
14.1	Introduction	85
14.2	Solid Solutions	86
14.3	Activity Coefficients in Solid Solutions	92
14.4	Summary	109

Online Materials: Additional Chapters from the Second Edition

15	Electrolyte Solutions	
15.1	Introduction	111
15.2	Activities of Electrolyte Components	111
15.3	Numerical Values for Single-Ion Properties	123
15.4	The Debye–Hückel Theory	127
15.5	Activity Coefficients of Neutral Molecules	134
15.6	Ion Association, Ion Pairs and Complexes	135
15.7	The Pitzer Equations	137
15.8	The HKF Model for Aqueous Electrolytes	138
15.9	Comparison of Pitzer and HKF Models	140
	The van 't Hoff Equilibrium Box	143
1.1	Introduction	143
1.2	The Affinity	144
1.3	The Two Kinds of Work	145
1.4	Irreversible Work	151
1.5	Summary	155
	Topics in Mathematics	156
C.1	Differentials and Derivatives	156
C.2	Partial Derivatives and Total Differentials	159
C.3	Integration	159
C.4	Single-Valued and Continuous Functions	160
C.5	Exact and Inexact Differentials	161
C.6	Homogeneous Functions	163
C.7	Euler's Theorem for Homogeneous Functions	164
C.8	Legendre Transforms	165
C.9	All Components in All Phases	170
C.10	Chemical Potentials of Dilute Components	175
C.11	The Bursting Balloon	176
	References	178

PREFACE

Why another book on thermodynamics?

I wrote the first edition of this book because *Thermodynamics in Geochemistry* (Anderson and Crerar, 1993) was not suitable for the teaching I was doing at the time, a second-year geochemistry course for geology specialists and geological engineers. I wanted something shorter and less detailed. Later I wanted to write something more suitable for my students and other graduate students, resulting in the second edition.

But then the first edition went out of print, and several people told me that it was better for teaching than the second edition, which was seen as more of a reference book despite the fact that it includes just about all of the first edition. So the objective with this edition is to make a book more like the first edition available again, that is, one more suitable for a first introduction to thermodynamics, though with many improvements. Several chapters and appendices of the second edition have been cut, and others made shorter and more concise. Because thermodynamic potentials are the central concept in chemical thermodynamics, the first four chapters extend the ball-in-valley analogy to introduce these, as well as exact and inexact differentials, considerably improving the introduction to thermodynamic theory. There is also an increased emphasis on the importance of field observations in the application of thermodynamics to natural systems.

The three editions of this book and *Thermodynamics in Geochemistry* have several features in common, besides the fact that they have an Earth science point of view, and regarding which they differ from other books on thermodynamics. These differences include the following points.

- Presentation of thermodynamics as a model or idealization of real systems.
- Emphasis on the significance of the fact that thermodynamics consists of single-valued continuous functions.
- An approach to entropy which avoids discussion of cycles and the entropy of the Universe: Gibbs, not Carnot/Clausius.
- Emphasis on the importance of metastable equilibrium states and thermodynamic constraints.
- Emphasis on the fact that time is not a thermodynamic variable.

The presentation is exclusively classical, meaning that statistical mechanics is barely mentioned; only equilibrium states and macroscopic variables are considered. Some consider this approach obsolete, believing that classical thermodynamics has largely been superseded by the greater explanatory power of statistical mechanics. Because of this, many books on thermodynamics, perhaps a majority, have a chapter or a section on statistical mechanics. Teachers of thermodynamics now commonly blend thermodynamics

Preface

and statistical mechanics together into a course in “thermal physics,” in which classical thermodynamics inevitably becomes subordinate (Callen, 1985, p. viii).

This is not the best approach for scientists and engineers dealing with real-world problems. Knowing that equilibrium requires that energy be distributed among the system’s degrees of freedom in a manner described by a Boltzmann distribution adds nothing useful for a geochemist investigating a waste disposal site or a metallic ore deposit. Gibbs said that the equilibrium state has no gradients in temperature, pressure, or composition, and that is entirely sufficient. What might help is the knowledge that in thermodynamics this state is an idealization, so it won’t exist at the disposal site and never existed at the ore deposit site, and that despite this thermodynamics will be essential in the study of such natural systems.

There is no doubt about the explanatory power of statistical mechanics, but, although a chapter or a section on statistical mechanics will give a general idea of the ideas involved, it is not sufficient for a good understanding; in fact, it is a distraction from a first attempt at learning thermodynamics. Statistical mechanics may well be in some sense more fundamental than classical thermodynamics, but more fundamental does not mean more useful. It is even possible to question whether thermodynamics can be reduced to statistical mechanics; whether concepts such as entropy in thermodynamics and statistical mechanics are the same or at least simply related (Sklar, 1993, p. 337), but such philosophical arguments are of even less concern to geochemists. In his book on statistical mechanics, Nash (1974) says

From a union of the entropy and energy concepts ... there was born a notably abstract science with innumerable concrete applications; a science of thermodynamics that combines magnificent generality with unflinching reliability to a degree unrivalled by any other science known to man.

It has not been superseded.

Geochemical Modeling

In common with other sciences, thermodynamics deals with idealized concepts, and there are always attempts to make it seem more realistic. It is better to teach and learn thermodynamics as it really is, with a clear distinction between real systems and the thermodynamic models of these systems. The connection between thermodynamics and reality is made, not by explaining entropy with statistical mechanics, but by using thermodynamics to elucidate the countless number of practical real-world problems in all aspects of Earth science – ore formation, chemical oceanography, the environment, most of igneous and metamorphic petrology, and so on. In this sense, doing exercises and problems is even more important than in other subjects. But it can be taken too far. There is a tendency to add realism by including topics such as fluid flow and reactive transport, the subjects of geochemical modeling programs such as the USGS program PHREEQC (Parkhurst and Appelo, 2013) or the programs in *The Geochemist’s Workbench* (2015). These applications greatly enhance the power of thermodynamics in practical

Preface

situations, and tech-savvy students love using them. The problem is that, much like the inclusion of statistical mechanics, including such programs dilutes the concentration on thermodynamics itself, and obscures the idea that thermodynamics itself is a model. An exception is the use of these programs to do speciation (Chapter 10), which greatly expands the ability of thermodynamics to deal with problems involving aqueous solutions. Having at least one course which deals only with classical equilibrium thermodynamics, with problem sets that must be done with a calculator or a spreadsheet, is the only way to really learn the subject.

Acknowledgments

There are many references in the text to data from Johnson *et al.* (1992), which in the second edition was referred to as SUPCRT92. These data have been superseded by data from THERMOCALC (Holland and Powell, 2011) but, as the data are used for illustrative purposes only, there was no point in recalculating all the results from SUPCRT92. I thank Roger Powell and Tim Holland for supplying data for those places where it seemed important.

It is a pleasure to acknowledge the encouragement and support of Dr. Norman Evensen in the writing of this book. His wide-ranging knowledge of science and mathematics provided valuable insights.

ONLINE RESOURCES AND EXERCISES

This book is intended as an introduction to thermodynamics. To give instructors the option of including other aspects of particular thermodynamic topics, several chapters and sections from the second edition (Anderson, 2005) are available on the Cambridge University Press website for this book, www.cambridge.org/thermodynamics.

These sections are as follows.

- Chapter 10 Real Solutions
- Chapter 11 The Phase Rule
- Chapter 13 Equations of State
- Chapter 14 Solid Solutions
- Chapter 15 Electrolyte Solutions
- The van 't Hoff Equilibrium Box
- Topics in Mathematics

At appropriate places in the text, reference to the additional information available online is noted in a box like this, on page 154:



Equations of State

The ideal gas equation $PV = nRT$ or $PV = RT$ is an equation of state; an equation relating the volume of an ideal gas to its pressure and temperature. For real gases there have been many modifications of this equation, and there are other equations of state which interrelate not only P , V , and T , but also thermodynamic parameters such as enthalpy, Gibbs energy, and entropy. See Chapter 13 Equations of State, in the online material.

Other boxes add worked examples or more details of the material in the text. For example on page 21 there is this:

Box 2.1 Scientific vs. Engineering Units

In science, *molar* properties, such as molar volumes and molar energies, are most commonly used. In engineering, on the other hand, *specific* properties are more common. Specific properties are mass-related rather than mole-related. Thus the specific volume of water at 25 °C is 1.0029 cm³ g⁻¹. Molar and specific properties are related by the molar mass (or so-called gram formula weight, gfw) of the substance. That for water is 18.0153 g mol⁻¹, so 1.0029 cm³ g⁻¹ × 18.0153 g mol⁻¹ = 18.068 cm³ mol⁻¹.

Exercises and Additional Problems

Exercises

At the end of each chapter there is a set of exercises on the material in that chapter under the heading **Exercises**. These are intended to be done by students as an aid to understanding, and the answers are in Appendix C.

Additional Problems

Following that, in most chapters under the heading **Additional Problems** there are more problems, often a bit more difficult, the answers to which are available to instructors from Cambridge University Press.