BASIC PHYSICAL CHEMISTRY FOR THE
ATMOSPHERIC SCIENCES
Second Edition

Modern studies of atmospheres, oceans, and Earth and planetary systems require a good knowledge of basic chemical principles. This book provides a clear, concise grounding in these principles. Undergraduate and graduate students with little formal training in chemistry can work through the chapters, and the numerous exercises, within this book before accessing more advanced texts in atmospheric chemistry, geochemistry, and the environmental sciences.

Basic Physical Chemistry for the Atmospheric Sciences covers the fundamental concepts of chemical equilibria, chemical thermodynamics, chemical kinetics, solution chemistry, acid and base chemistry, oxidation-reduction reactions, and photochemistry. This new edition has been updated and revised from the first edition.

In a companion volume entitled Introduction to Atmospheric Chemistry (2000, Cambridge University Press) Peter Hobbs provides an introduction to atmospheric chemistry itself, including its applications to air pollution, acid rain, the ozone hole, and climate change. Together these two books provide an ideal introduction to atmospheric chemistry for a variety of disciplines.

Peter V. Hobbs (University of Washington) is known internationally for his research on many aspects of the atmosphere: clouds, precipitation, aerosols, storms, atmospheric chemistry, and climate. He is the author of the definitive text Ice Physics, the author of Introduction to Atmospheric Chemistry (Cambridge University Press, 2000), co-author (with J. M. Wallace) of one of the most widely used textbooks in meteorology Atmospheric Sciences: An Introductory Survey, and editor of several other books. He has authored more than 300 scientific papers. Professor Hobbs has served on many national and international committees, including the Scientific Steering Committee of the International Global Atmospheric Chemistry Program, and international scientific bodies. He has been a visiting senior research scientist in England, France, Germany and Italy.
BASIC PHYSICAL CHEMISTRY FOR THE ATMOSPHERIC SCIENCES
SECOND EDITION

A Companion Text to “Introduction to Atmospheric Chemistry”

PETER V. HOBBS
University of Washington
Contents

Preface to first edition ix
Preface to second edition xi

1 Chemical equilibrium 1
   1.1 Some introductory concepts 1
   1.2 Equilibrium constants 3
   1.3 Reaction quotient 8
   1.4 LeChatelier’s principle 10
      Exercises 12

2 Chemical thermodynamics 17
   2.1 The first law of thermodynamics; enthalpy 17
   2.2 Enthalpies of reaction and formation 21
   2.3 Entropy and the second law of thermodynamics 22
   2.4 The third law of thermodynamics; absolute entropies 26
   2.5 Criteria for equilibrium and spontaneous transformation 27
   2.6 Standard free energy changes 29
   2.7 Free energy change and the equilibrium constant 31
   2.8 Chemical potential; homogeneous nucleation of water-vapor condensation 34
      Exercises 38

3 Chemical kinetics 43
   3.1 Reaction rates 43
   3.2 Reaction mechanisms 46
   3.3 Reaction rates and equilibria 50
   3.4 Collision theory of gaseous reactions 52
3.5 The effect of temperature on reaction rates: the Arrhenius’ relation
3.6 Catalysis
3.7 Half-life, residence time, and renewal time

Exercises

4 Solution chemistry and aqueous equilibria
4.1 Definitions and types of solutions
4.2 Solution concentrations
4.3 Factors affecting solubility
4.4 Colligative properties
4.5 Aqueous solutions; electrolytes
4.6 Aqueous equilibria
4.7 Strong and weak electrolytes; ion-product constant for water

Exercises

5 Acids and bases
5.1 Some definitions and concepts
5.2 The nature of H⁺(aq)
5.3 The Brønsted-Lowry theory; conjugate acid-base pairs
5.4 Strengths of acids and bases; acid-dissociation (or ionization) constant
5.5 The Lewis theory
5.6 The pH scale
5.7 Polyprotic acids
5.8 Hydrolysis
5.9 Buffers
5.10 Complex ions
5.11 Mass balance and charge balance relations
5.12 The pH of rainwater

Exercises

6 Oxidation–reduction reactions
6.1 Some definitions
6.2 Oxidation numbers
6.3 Balancing oxidation–reduction reactions
6.4 Half-reactions in electrochemical cells
6.5 Strengths of oxidants and reductants; standard cell and half-cell potentials
### Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.6</td>
<td>Standard cell potentials and free-energy change</td>
<td>124</td>
</tr>
<tr>
<td>6.7</td>
<td>The Nernst equation</td>
<td>126</td>
</tr>
<tr>
<td>6.8</td>
<td>Redox potentials; Eh–pH diagrams</td>
<td>128</td>
</tr>
<tr>
<td>6.9</td>
<td>Gram-equivalent weight and normality</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td><strong>Exercises</strong></td>
<td>132</td>
</tr>
<tr>
<td>7</td>
<td>Photochemistry</td>
<td>137</td>
</tr>
<tr>
<td>7.1</td>
<td>Some properties of electromagnetic waves</td>
<td>137</td>
</tr>
<tr>
<td>7.2</td>
<td>Some photochemical terminology and principles</td>
<td>139</td>
</tr>
<tr>
<td>7.3</td>
<td>Quantum yields</td>
<td>141</td>
</tr>
<tr>
<td>7.4</td>
<td>Rate coefficients for photolysis</td>
<td>143</td>
</tr>
<tr>
<td>7.5</td>
<td>Photostationary states</td>
<td>145</td>
</tr>
<tr>
<td>7.6</td>
<td>Stratospheric ozone and photochemistry; depletion of stratospheric ozone</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td><strong>Exercises</strong></td>
<td>154</td>
</tr>
<tr>
<td>Appendix I</td>
<td>International system of units (SI)</td>
<td>159</td>
</tr>
<tr>
<td>Appendix II</td>
<td>Some useful numerical values</td>
<td>160</td>
</tr>
<tr>
<td>Appendix III</td>
<td>Atomic weights</td>
<td>161</td>
</tr>
<tr>
<td>Appendix IV</td>
<td>Equilibrium (or dissociation) constants for some chemical reactions</td>
<td>164</td>
</tr>
<tr>
<td>Appendix V</td>
<td>Some molar standard Gibbs free energies of formation, molar standard enthalpies (or heats) of formation, and molar absolute entropies at 25°C and 1 atmosphere</td>
<td>169</td>
</tr>
<tr>
<td>Appendix VI</td>
<td>Names, formulas, and charges of some common ions</td>
<td>172</td>
</tr>
<tr>
<td>Appendix VII</td>
<td>Answers to exercises and hints and solutions to selected exercises</td>
<td>173</td>
</tr>
<tr>
<td>Index</td>
<td></td>
<td>187</td>
</tr>
</tbody>
</table>
Preface to first edition

A short account of the origins of this book will explain its purpose. In the 1970s I coauthored (with John M. Wallace) a textbook for senior undergraduates and first-year graduate students entitled *Atmospheric Science: An Introductory Survey* (Academic Press, 1977). At the time that text was written it was not considered necessary to include a chapter on atmospheric chemistry. By the early 1990s, when we began to think about a second edition of *Atmospheric Science*, the importance of atmospheric chemistry was such that it was inconceivable that such a book would not include a substantial chapter on this subject.

In the intervening years I had introduced a section on atmospheric chemistry into the survey course taken by all first-year graduate students in the Atmospheric Sciences Department at the University of Washington. I quickly discovered, however, that many of the students either had no previous instruction in chemistry or had long since forgotten what little they had known. I therefore wrote an (unpublished) primer on physical chemistry for these students; the present book grew out of that primer.

Reviewed herein are some of the fundamental concepts associated with chemical equilibrium, chemical thermodynamics, chemical kinetics, aqueous solutions, acid–base chemistry, oxidation–reduction reactions and photochemistry, all of which are essential to an understanding of atmospheric chemistry. The approach is primarily from the macroscopic viewpoint, which provides the tools needed by the pragmatist. A deeper understanding requires extensive treatment of the electronic structure of matter and chemical bonding, topics that are beyond the scope of this introductory text. This book can be used for either self-instruction, or as the basis for a short introductory class on chemistry, prior to courses in which chemistry is applied to one of the geosciences. In addition to
Preface to first edition

students (and I use this term in its broadest sense) of atmospheric sciences, I hope this book will be useful to others. It should be suitable, for example, as a precursor to undergraduate and graduate courses in which chemistry is applied to any of the geosciences and environmental sciences.

In keeping with the didactic approach of this book, and the view that any science is best learned by solving problems, I have provided solutions to 50 exercises in the text and posed 112 exercises for the student. Answers to all the quantitative problems, and hints and solutions to selected problems, are given in Appendix VII.

In preparing this book I benefited from the following texts, which are recommended to the reader: Chemistry: An Experimental Science edited by G. C. Pimentel (W. H. Freeman, 1963) gives a broad introduction to chemistry with emphasis on its experimental foundations; Chemistry: The Central Science by T. L. Brown and H. E. LeMay Jr. (Prentice-Hall Inc., 1981) and General Chemistry: Principles and Modern Applications by R. H. Petrucci (Macmillan Pub. Co., 1982) provide more extensive accounts of most of the topics discussed in the present book and deal with many other aspects of chemistry. Finally, for the student who wants to take the next step in chemistry beyond that presented here, University Chemistry by B. H. Mahan (Addison-Wesley, 1965) is highly recommended.

This book was started in 1984 when I was an Alexander von Humboldt Foundation Senior Scientist in Germany, and it was essentially finished in 1993 during a sabbatical at the Instituto FISBAT-CNR, Bologna, Italy. Thanks are due to both of these organizations for their generous support. It is also a pleasure to thank my colleagues Professors Dean Hegg and Conway Leovy, and many students, particularly John Herring and Cathy Cahill, who commented on various drafts of this book and made suggestions for its improvement. I am grateful to the National Science Foundation for supporting my own research in atmospheric chemistry over many years.

Any suggestions or corrections related to this book will be gratefully received.

Seattle
May 1994
Preface to second edition

The success of the first edition of this book encouraged me to write a companion text entitled Introduction to Atmospheric Chemistry (Cambridge University Press, 2000). On the occasion of the publication of the latter text, the opportunity has been taken to issue a second edition of Basic Physical Chemistry for the Atmospheric Sciences.

In this second edition a number of minor (and a few major) errors have been corrected, and the text has been clarified in several places. I hope that, taken together, these two companion volumes will provide students, researchers, and even the interested layperson, with a sound introduction to the fascinating subject of atmospheric chemistry, which has emerged as a discipline in its own right in just the past few decades.

Comments on this book, which will be gratefully received, can be sent by e-mail to: phobbs@atmos.washington.edu. Current information on the book, including any errata, can be found on http://cargsun2.atmos.washington.edu/~debbie/HobbsWebPage/BasicChem/Info.html.

Peter V. Hobbs