

A1099

Hálinho's
Lond

8071

PRINCIPLES AND APPLICATIONS OF GEOCHEMISTRY

A Comprehensive Textbook for Geology Students

Second Edition

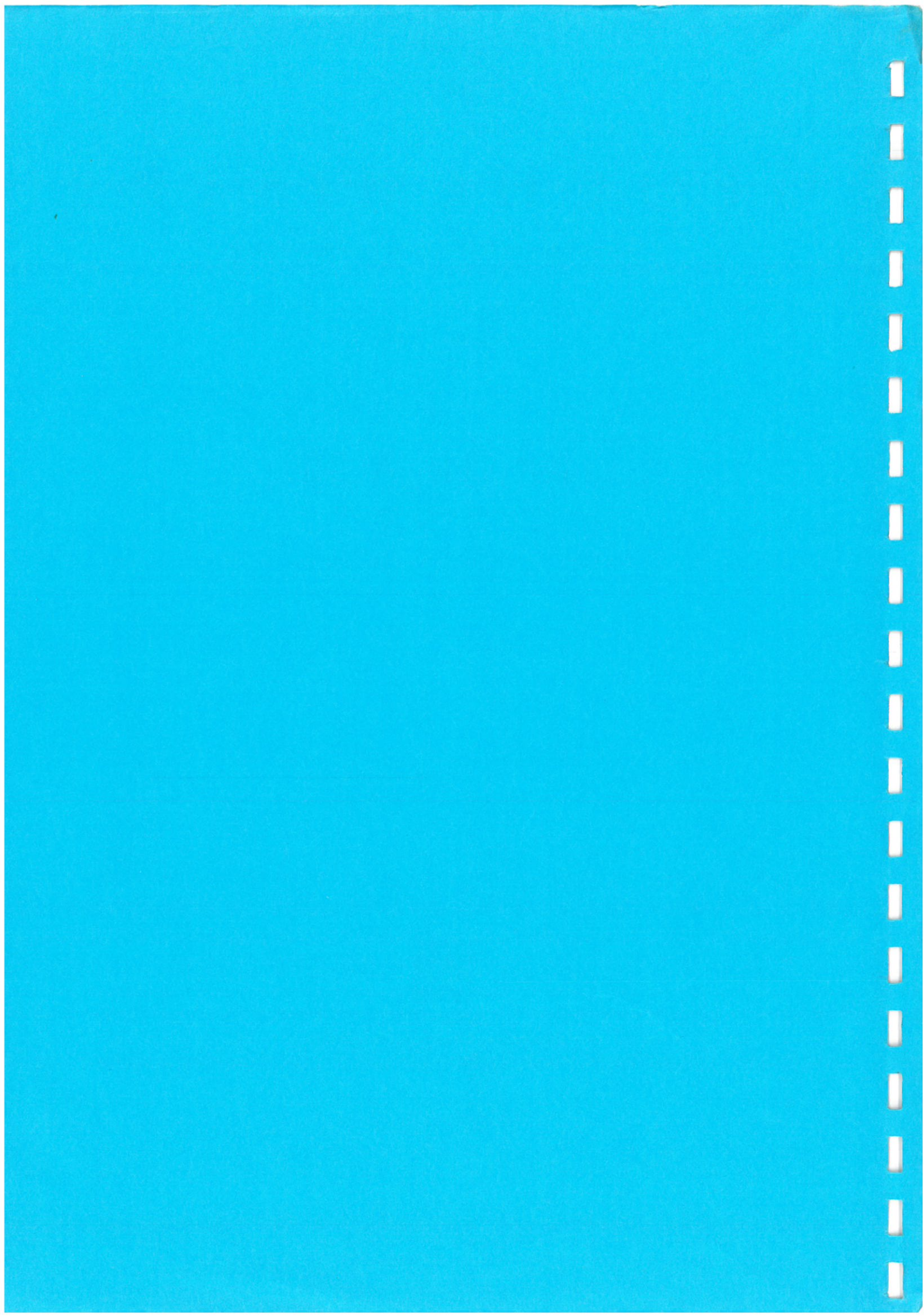
H Geow
793

GUNTER FAURE

THE OHIO STATE UNIVERSITY



Prentice Hall
Upper Saddle River, New Jersey 07458



A1049

Palin's
Lore

8071

PRINCIPLES AND APPLICATIONS OF GEOCHEMISTRY

A Comprehensive Textbook for Geology Students

Second Edition

H Geow
793

GUNTER FAURE

THE OHIO STATE UNIVERSITY



Prentice Hall
Upper Saddle River, New Jersey 07458

Library of Congress Cataloging-in-Publication Data

Faure, Gunter.

Principles and applications of geochemistry : a comprehensive textbook for geology students/Gunter Faure.—2nd ed.

p. cm.

Rev. ed. of: Principles and applications of inorganic geochemistry. c1991.

Includes bibliographical references and index.

ISBN 0-02-336450-5

I. Geochemistry I. Faure, Gunter. Principles and applications of inorganic geochemistry. II. Title.

QE515.F28 1998

551.9—dc21

97-44563

CIP

Executive Editor: Robert A. McConnin
Total Concept Coordinator: Kimberly P. Karpovich
Art Director: Jayne Conte
Cover Designer: Karen Salzbach
Manufacturing Manager: Trudy Piscioti
Production Supervision/Composition: WestWords, Inc.



©1998, 1991 by Prentice-Hall, Inc.
Simon & Schuster/A Viacom Company
Upper Saddle River, New Jersey 07458



All rights reserved. No part of this book may be reproduced, in any form or by any means, without permission in writing from the publisher.

Printed in the United States of America

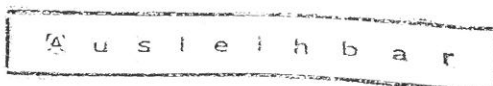
10 9 8 7 6 5 4 3 2

ISBN 0-02-336450-5

ISBN 0-02-336450-5



Prentice-Hall International (UK) Limited, *London*
Prentice-Hall of Australia Pty. Limited, *Sydney*
Prentice-Hall Canada Inc., *Toronto*
Prentice-Hall Hispanoamericana, S.A., *Mexico*
Prentice-Hall of India Private Limited, *New Delhi*
Prentice-Hall of Japan, Inc., *Tokyo*
Simon & Schuster Asia Pte. Ltd., *Singapore*
Editora Prentice-Hall do Brasil, Ltda., *Rio de Janeiro*



For Terri

Contents

Preface xiii

Part I

PLANET EARTH IN THE SOLAR SYSTEM

1

What Is Geochemistry? 2

1.1 Early History	2
1.2 Geochemistry in the U.S.S.R.	3
1.3 V. M. Goldschmidt	4
1.4 Modern Geochemistry	5
References	7

2

In the Beginning 8

2.1 The Big Bang	8
2.2 Stellar Evolution	11
2.3 Nucleosynthesis	13
2.4 Summary	20
Problems	20
References	20

3

The Solar System 22

3.1 Origin of the Solar System	22
3.2 Origin of the Earthlike Planets	25
3.3 Satellites of the Outer Planets	26
3.4 Pictures of Our Solar System	29
3.5 Summary	42
References	42

4

Chemical Differentiation of the Earth 43

4.1 Internal Structure of the Earth	43
4.2 The Continental Crust: Major Elements	46

4.3 Differentiation of Igneous and Sedimentary Rocks	49
4.4 Differentiation of the Hydrosphere	52
4.5 Summary	56
Problems	57
References	57

Part II

PRINCIPLES OF INORGANIC GEOCHEMISTRY

5

The Electronic Structure of Atoms 60

5.1 The Atom of Thomson and Rutherford	60
5.2 Bohr's Theory of the Hydrogen Atom	61
5.3 Emission of X-rays	63
5.4 Schrödinger's Model of the Atom	64
5.5 The Aufbau Principle	67
5.6 Summary	69
Problems	72
References	72

6

The Periodic Table and Atomic Weights 74

6.1 Mendeleev's Periodic Table	74
6.2 The Modern Periodic Table	74
6.3 Basic Principles of Atomic Physics	77
6.4 Atomic Weights	78
6.5 Summary	81
Problems	82
References	82

7
**Chemical Bonds, Ionic Radii,
 and Crystals 83**

7.1 Electron Donors Versus Acceptors	83
7.2 Measures of Metallic Character	84
7.3 Bonding in Molecules	87
7.4 Ionic Crystals	89
7.5 Ionic Radii	91
7.6 Summary	97
Problems	97
References	98

8
**Ionic Substitution in
 Crystals 99**

8.1 Goldschmidt's Rules of Substitution	99
8.2 Camouflage, Capture, and Admission	100
8.3 Coupled Substitution: Key to the Feldspars	102
8.4 Distribution Coefficients and Geothermometers	103
8.5 Geochemical Classification of the Elements	105
8.6 Summary	106
Problems	108
References	108

Part III

**AQUEOUS GEOCHEMISTRY AND
 THE STABILITY OF MINERALS**

9
Acids and Bases 110

9.1 Chemical Reactions and Equilibria	110
9.2 The Law of Mass Action	112
9.3 Dissociation of Weak Acids and Bases	114
9.4 Solubility of Sparingly Soluble Bases	121

9.5 pH Control of Dissociation Equilibria	123
9.6 Solubility of Amorphous Silica	124
9.7 Summary	127
Problems	128
References	128

10
Salts and Their Ions 130

10.1 Solubility of Salts	130
10.2 Hydrolysis	137
10.3 Activities and Concentrations	139
10.4 Solubility of Calcium Carbonate	142
10.5 Chemical Weathering	148
10.6 Transformation of Potassium Feldspar to Kaolinite	149
10.7 Summary	152
Problems	153
References	153

11
Thermodynamics 155

11.1 Definitions	155
11.2 The First Law	157
11.3 Enthalpy	157
11.4 Heats of Reaction	159
11.5 Heat Capacity	160
11.6 The Second Law	161
11.7 Gibbs Free Energy	163
11.8 Derivation of the Law of Mass Action	165
11.9 Fugacity and Activity	166
11.10 The van't Hoff Equation	168
11.11 Solubility of Amorphous Silica Between 0 and 100 °C	168
11.12 Summary	169
Problems	170
References	171

12
Mineral Stability Diagrams 172

12.1 Chemical Weathering of Feldspars	172
12.2 Formation of Zeolites	182
12.3 Magnesium Silicates	186

12.4 Solubility Diagrams	190
12.5 Fugacity Diagrams	194
12.6 Summary	198
Problems	199
References	199

13

Clay Minerals 200

13.1 Crystal Structure	200
13.2 Classification and Chemical Composition	202
13.3 Gibbs Free Energies of Formation	208
13.4 Stability Diagrams	211
13.5 Colloidal Suspensions and Ion Exchange	217
13.6 Dating of Clay Minerals	221
13.7 Summary	222
Problems	223
References	224

14

Oxidation-Reduction Reactions 226

14.1 Balancing Equations of Oxidation-Reduction Reactions	226
14.2 The Electromotive Series	229
14.3 The Emf of Electrochemical Cells	234
14.4 Stability Limits of Water in Terms of Eh and pH	235
14.5 Stability of Iron Compounds	238
14.6 Summary	249
Problems	251
References	252

15

Rates of Geochemical Processes 253

15.1 Rates of Chemical Reactions	253
15.2 Transport of Matter: Advection	257
15.3 Transport of Matter: Diffusion	259
15.4 Growth of Concretions During Diagenesis	263
15.5 Growth of Monomineralic Layers	268
15.6 Summary	271

Problems	271
References	273

Part IV**ISOTOPE GEOCHEMISTRY AND MIXING**

16

Isotopic Geochronometers 276

16.1 Decay Modes	276
16.2 Law of Radioactivity	281
16.3 Methods of Dating	284
16.4 Cosmogenic Radionuclides	292
16.5 Summary	297
Problems	297
References	299

17

Isotope Fractionation 301

17.1 Principles of Isotope Fractionation	301
17.2 Mathematical Relations	304
17.3 Isotope Fractionation in the Hydrosphere	306
17.4 Oxygen Isotope Composition of Calcite	308
17.5 Oxygen and Hydrogen in Clay Minerals	311
17.6 Groundwater and Geothermal Brines	313
17.7 Isotope Fractionation of Carbon	315
17.8 Isotope Compositions of Strontium in Carbonate Rocks	317
17.9 Isotope Fractionation of Sulfur	319
17.10 Summary	323
Problems	325
References	325

18

Mixing and Dilution 328

18.1 Binary Mixtures	328
18.2 Dilution	330

X CONTENTS

18.3	Evaporative Concentration	331	20.3	Chemical Composition of Meteoric Precipitation	375
18.4	Ternary Mixtures	332	20.4	Normative Minerals from Water Compositions	376
18.5	Isotopic Mixtures of One Element	335	20.5	Evaporative Concentration	383
18.6	Isotopic Mixtures of Two Elements	337	20.6	Water Quality	392
18.7	Summary	338	20.7	Summary	395
	Problems	339		Problems	396
	References	340		References	397

Part V

APPLICATIONS OF GEOCHEMISTRY TO THE SOLUTION OF GLOBAL PROBLEMS

19

Consequences of Chemical Weathering 342

19.1	Changes in Chemical Composition of Rocks	343
19.2	Normative Mineral Composition of Weathering Products	345
19.3	Susceptibility of Minerals to Weathering	347
19.4	Formation of Placer Deposits	351
19.5	Provenance Determination by Isotopic Dating	353
19.6	Formation of Soils	354
19.7	Geomicrobiology	358
19.8	Food Production and Population Growth	361
19.9	Summary	363
	Problems	364
	References	365

20

Chemical Composition of Surface Water 368

20.1	Chemical Analysis of Water in Streams	368
20.2	Chemical Composition of Streams	370

21

Chemical Weathering of Mineral Deposits 400

21.1	Metallic Mineral Deposits	400
21.2	Oxidation of Iron Sulfides and the Role of Bacteria	401
21.3	Eh-pH Diagram for Copper Minerals	403
21.4	Supergene Enrichment of Fe-Cu Sulfide Deposits	407
21.5	Replacement of Pyrite by Chalcocite	408
21.6	Oxidation of Ore Minerals of Other Metals	411
21.7	Geochemical Exploration	413
21.8	Production and Consumption of Mineral Resources	417
21.9	Summary	421
	Problems	422
	References	423

22

Geochemical Cycles 425

22.1	The Principle of Mass Balance	426
22.2	Mass Balance for Major Elements in the Ocean	428
22.3	Mass Balance for Trace Elements in the Ocean	431
22.4	The Cycles of C-H-O-N	433
22.5	The Sulfur Cycle	443
22.6	Summary	446
	Problems	447
	References	447

23	
Chemistry of the Atmosphere	449
23.1 Structure and Composition	450
23.2 Ultraviolet Radiation	451
23.3 Ozone in the Stratosphere	452
23.4 Ozone Hole over Antarctica	453
23.5 Infrared Radiation and the Greenhouse Effect	455
23.6 Prediction of the Future Global Climate	457
23.7 Summary	458
Problems	459
References	459

24	
Environmental Geochemistry:	
Disposal of Radioactive Waste	461
24.1 The Big Picture	461
24.2 High-Level Nuclear Waste Disposal	462
24.3 Geological Disposal of Radioactive Waste	465
24.4 Geochemistry of Plutonium	468
24.5 Eh-pH Diagrams of Neptunium and Plutonium	473
24.6 Analog Studies: The Natural Reactors at Oklo, Gabon	476
24.7 Reactor Accidents: Chernobyl, Ukraine	478
24.8 Summary	481
Problems	482
References	483

25	
Effect of Environmental Lead on Human Health	485
25.1 Isotope Composition of Environmental Lead	485
25.2 Lead in the Environment	487
25.3 Lead in Plants	492
25.4 Lead Poisoning of Cows and Horses	495
25.5 Human Bones and Tissues	497
25.6 Lead in the Bones of Ancient Peoples	499
25.7 Summary	502
Problems	503
References	504

Appendix A	
Compilations of Geochemical Data	506

Appendix B	
Standard Gibbs Free Energies (G_f°) and Standard Enthalpies of Formation (H_f°)	519

Author Index	575
---------------------	------------

Subject Index	589
----------------------	------------

Preface

This textbook is intended as an *introduction to geochemistry* for geology students in their senior year or in their first year of graduate work. At that time in their education, students are ready to *relearn* those principles of chemistry that are especially applicable to the study of geological processes. Geochemistry can enhance their understanding of these processes and can teach them to apply principles of chemistry to the solution of geological problems. Geologists in virtually all branches of the science can benefit from an introductory course in geochemistry because it can help them to make quantitative predictions about the outcome of chemical reactions that occur in the context of many geological processes.

The subject matter of this book is presented in five parts. Part I: Planet Earth in the Solar System (Chapters 1 through 4) presents the big picture starting with the Big Bang, stellar evolution, nucleosynthesis, the solar system, and the geochemistry of the Earth. This part also contains a brief history of geochemistry leading up to a statement of its goals and stating the theme of this book: Studies of geochemistry convert idle speculation into understanding.

The second part, Principles of Inorganic Geochemistry (Chapters 5 through 8), starts with the electronic structure of atoms and demonstrates how wave mechanics and the Aufbau principle lead directly to the periodicity of the chemical properties of the elements. Once the periodic table has been constructed, systematic variations in bonding, ionic radii, and the structure of crystals become apparent, thus preparing the way for a discussion of ionic substitution based on the rules of Goldschmidt and Ringwood. Part II concludes with discussions of coupled substitution in feldspar, distribution coefficients, and the geochemical classification of the elements.

Part III is entitled Aqueous Geochemistry and the Stability of Minerals (Chapters 9 through 15).

These chapters explain the concept of chemical equilibrium and use the Law of Mass Action to study the dissociation of weak acids and bases and to calculate the solubility of amorphous silica as a function of the pH. Next, the dissociation of salts, the hydrolysis of their ions, and the necessity of using the activities of ions rather than their molal concentrations in Mass Action problems are presented. All of these concepts come into play in the carbonate equilibria involving calcite, its ions in aqueous solution, and CO_2 in the atmosphere. However, the incongruent dissolution of microcline to form kaolinite plus ions leads to an impasse because the value of the equilibrium constant for that reaction has not been measured.

Therefore, Chapter 11 contains a guided tour of the principles of thermodynamics leading up to a derivation of the Law of Mass Action for reacting mixtures of ideal gases at equilibrium. In addition, this chapter demonstrates that equilibrium constants at the standard temperature and pressure can be calculated from the Gibbs free energy change of chemical reactions. This skill is immediately used to construct ion-activity diagrams for aluminosilicate minerals including zeolites (Chapter 12) and clay minerals (Chapter 13).

Finally, oxidation-reduction reactions are introduced in Chapter 14, and the previously acquired knowledge of thermodynamics is used to explain some basic principles of electrochemistry. These insights are then used to define the stability limits of water on the Earth and to construct Eh-pH diagrams for the oxides of iron and their ions. Chapter 15 deals with the kinetics of chemical reactions, and with the transport of ions by diffusion and advection. These concepts are used to model the growth of concretions during diagenesis and the formation of monomineralic layers at the sediment-water interface.

Part IV is entitled Isotope Geochemistry and Mixing (Chapters 16 through 18). Following

the presentation of the different modes of decay and a statement of the Law of Radioactivity, Chapter 16 continues with the derivation of the geochronometry equation based on the accumulation of stable radiogenic daughter nuclides. This equation is then used to explain the principles and assumptions of dating by the K–Ar, Rb–Sr, Sm–Nd, Re–Os, and U, Th–Pb methods. In addition, the chapter contains descriptions of the $^{230}\text{Th}/^{238}\text{U}$ method of measuring sedimentation rates and of dating by the cosmogenic radionuclides ^{14}C , ^{10}Be , and ^{26}Al .

Chapter 17 is devoted to the fractionation of the stable isotopes of H, O, C, and S in nature. This chapter includes derivations of the basic mathematical relationships used to interpret variations of the isotope compositions of meteoric water, marine calcite, clay minerals, oilfield brines, hydrocarbons, and sulfide minerals. In addition, Chapter 17 presents a discussion of the time-dependent variation of the isotope compositions of Sr and S in marine carbonates of Phanerozoic age and the use of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for dating Cenozoic marine carbonates.

Part IV concludes with Chapter 18 on mixing and dilution of water and sedimentary rocks that are mixtures of two or three components having different chemical compositions. The chapter continues with two-component mixtures containing elements having distinctive isotope compositions (Sr, Pb, O, H, etc.). The systematics of such mixtures are briefly illustrated using oilfield brines formed by mixing two components having different $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations.

The fifth and last part of this book is entitled Applications of Geochemistry to the Solution of Global Problems (Chapters 19 through 25). This part treats the consequences of chemical weathering of rocks, such as the formation of soils and their agricultural productivity (Chapter 19); the chemical composition of surface water, its evolution by evaporative concentration, and its contamination by natural and anthropogenic causes (Chapter 20); and the weathering of metallic mineral deposits based on Eh–pH diagrams and including a section on the importance of bacteria in the oxidation of iron sulfides (Chapter 21). The

resulting release of metals into the environment is the basis for geochemical methods of prospecting. The chapter ends with a discussion of mineral economics including King Hubbert's prediction of the ultimate depletion of finite and nonrenewable resources such as petroleum.

The migration of ions released by weathering of rocks and metallic mineral deposits on the continents leads to a consideration of geochemical cycles in Chapter 22. After presenting the concept of mass balance, this chapter contains summaries of the geochemical cycles C–H–O–N, including water. The links between the reservoirs of these and other elements play an important role in stabilizing the chemical composition of the atmosphere and the oceans.

Chapter 23 on the chemistry of the atmosphere continues this train of thought by presenting the basic facts about the structure and chemical composition of the atmosphere. This information is then used to explain the formation of ozone in the stratosphere and its destruction by anthropogenic emissions of Cl-bearing gases, especially over Antarctica. The chapter also contains a presentation of the radiation balance of the Earth and the perturbation of this balance by emissions of gases that enhance the absorption of infrared radiation in the atmosphere. Chapter 23 ends with a long-range forecast of the effects of global warming on the time scale of 10^4 years based on the work of W. S. Broecker.

The dangers of environmental contamination are illustrated in Chapter 24 by consideration of the problems associated with high-level radioactive waste generated by nuclear reactors. The chapter explains how this waste is generated and how it is (or should be) processed prior to permanent storage in underground repositories. The geochemical properties of the transuranium elements, which play an important role in the long-term safety of such repositories, are briefly discussed using Eh–pH diagrams for neptunium and plutonium. Chapter 24 ends with a summary of the events and consequences of the explosion of a nuclear reactor in Chernobyl, Ukraine, on April 26, 1986.

The final chapter summarizes the geochemistry of Pb in the environment and its effect on

human health. Lead is dispersed primarily through the atmosphere in the form of aerosol particles. Some civilizations have suffered the consequences of Pb toxicity because this metal was used as a food additive and in household utensils. The effects of Pb poisoning on humans are subtle and difficult to identify because all humans alive today are contaminated with Pb released primarily because of its use as an additive in gasoline. The impairment of mental functions as well as the toxic effects of Pb were tragically demonstrated by the members of Sir John Franklin's expedition to the Canadian Arctic in 1845-47.

The presentation of the subject matter in this book starts with *basic principles* and *emphasizes quantitative* methods of problem solving in order to gain better *understanding* of natural phenomena. Although this book is intended to be an *introduction* to geochemistry, the references at the end of each chapter will permit students to pursue topics of their choice in the library and thereby approach the *state of the art*. In addition, the end-of-chapter problems enable students to test their understanding of the principles. The book ends with a compilation of geochemical data in Appendix A and of *thermodynamic data* for a large number of elements and their compounds in Appendix B. In addition, most chapters contain data tables and diagrams that will make the book a *useful source of geochemical data*. The diagrams have lengthy captions that should *encourage browsing* and will help users to extract information from them without necessarily having to reread the entire chapter.

This geochemistry text demonstrates that the principles and applications of geochemistry are internally consistent, useful for understanding the world around us, and accessible to anyone willing to make the effort. In addition, this book makes the point that geochemists have an important task to perform in society by assisting in the prudent use of natural resources and in the safe disposal of the resulting waste products.

In conclusion, I thank the reviewers who read the manuscript of this book and made many suggestions which helped me to improve it: James H. Crocket, McMaster University; William J. Green,

Miami University (Ohio); Donald I. Siegel, Syracuse University; Robert D. Shuster, University of Nebraska, Omaha; and A. Russell Flegal, University of California, Santa Cruz. The second edition has benefited significantly from comments by colleagues who have pointed out errors of various kinds in the first edition and suggested improvements in the presentation of the subject matter. I thank these individuals by name in alphabetical order: Walther M. Barnard, Georges Beaudoin, Phillip Boger, Daniel Marcos Bonotto, Steven E. Bushnell, Christopher Conaway, Ethan L. Grossman, Giehyeon Lee, Peter C. Lichtner, James O'Neil, Risto Piispanen, Robert D. Shuster, and Terri L. Woods. I also thank Robert A. McConnin, Executive Editor of Prentice Hall, for his interest in this book, Elisabeth H. Belfer for her role in its production, and Susan M. McMullen for drafting the diagrams of the first edition. I am grateful to Betty Heath for typing part of the manuscript for the second edition.

The ultimate purpose of this book is to encourage students of the Earth to adopt the quantitative approach to problem solving that is exemplified by geochemistry, and to make them aware of the important role Earth scientists must play in the effort to preserve our habitat on the Earth.

GUNTER FAURE

Postscript: A manual with solutions to the end-of-chapter problems is available to instructors from the publisher by writing on school stationery to the Geology Editor, Prentice Hall, 1 Lake Street, Upper Saddle River, NJ 07458.

PLANET EARTH IN THE SOLAR SYSTEM

Future generations may remember the 20th century primarily for the advances in technology that have enabled us to begin the exploration of the solar system. Our resulting awareness of the celestial environment of the Earth has raised questions about the origin and evolution of the solar system, of the Milky Way Galaxy, and of the Universe at large. The start of an introductory geochemistry course is an appropriate time to satisfy our desire to know the origins of the world in which we live.

What Is Geochemistry?

Geology began when early man first picked up a stone, considered its qualities, and decided that it was better than the stone he already had. Good stones were useful and they were collected, mined, and traded.

HENRY FAUL AND CAROL FAUL (1983, p. 1)

Geochemistry is based on the urge to understand why some stones are "good" and how they formed. It involves applications of the principles of chemistry to the solution of geological problems and therefore could not develop until chemistry and geology had been established as scientific disciplines. These applications were practiced first during the 16th century in the mines of Europe where knowledge of minerals and their chemical compositions was used to recognize and follow veins of ore. For example, in 1574 Lazarus Ercker, the superintendent of mines for King Rudolf II of Austria, published a manual in which he described ores and outlined procedures for their analysis (Ercker, 1951). However, several centuries passed before geochemistry in the present sense of the word became established as an integral component of Earth and Planetary Science.

1.1 Early History

Two essential prerequisites for the growth of geochemistry were the discovery of the chemical elements and the development of sensitive and accurate methods for the analysis of rocks and minerals. Until the end of the 16th century matter was thought to consist of earth, water, fire, and air, whose basic qualities were described as

warm, cold, dry, and wet. The metals gold, silver, copper, iron, tin, mercury, and lead together with sulfur and carbon had been known for thousands of years but were not recognized as elements in the present sense of the word. Antimony, arsenic, bismuth, and phosphorus were studied by the alchemists during the Middle Ages.

The development of analytical chemistry during the 18th century resulted in the discovery of 46 chemical elements between 1720 and 1850. After Bunsen and Kirchhoff invented the optical emission spectrograph, 30 additional elements were added from 1850 to 1925. The transuranium elements and certain other radioactive elements were discovered later in the 20th century (Correns, 1969).

As the number of known chemical elements increased during the 19th century, chemists became aware that they could be organized into groups based on similarities of their chemical properties. These tendencies became the foundation of the periodic table of the elements proposed independently by D. I. Mendeleev in 1869 and by J. L. Meyer in 1870 (Asimov, 1965). The cause for the periodicity of the chemical properties of the elements was not known then and was recognized only after the internal structure of atoms was worked out during the first 30 years of the 20th century.

The periodic table is a manifestation of the relationship between the internal structure of atoms and the chemical and physical properties of the elements. It facilitates a rational explanation of the chemical properties of the elements and of their observed distribution in nature.

The roots of geochemistry lie mainly in the 19th century, but it acquired its present multifaceted complexity during the 20th century. The word *geochemistry* was first used in 1838 by Christian Friedrich Schönbein, who was a chemistry professor at the University of Basel in Switzerland. The term was used again in 1908, 70 years later, when Frank W. Clarke of the U.S. Geological Survey published the first edition of his book, *The Data of Geochemistry*.

Clarke was the Chief Chemist of the U.S. Geological Survey from 1884 until 1925. He started the tradition for excellence in the analysis of rocks and minerals that has helped to make the Survey one of the largest geochemical research centers in the world. The first edition of Clarke's book was amazingly modern in its approach to geochemistry. He opened with chapters on the chemical elements, the atmosphere, lakes and rivers, and the ocean followed by chapters on saline lakes and springs and on evaporite deposits. Next he took up volcanic gases, magma, rock-forming minerals, and igneous rocks and then weathering, sedimentary rocks, metamorphic rocks, and ore deposits. The book ends with chapters on fossil fuels and their origin. That is pretty much how we would present the data of geochemistry today, but Clarke did it this way in 1908! More than 15 years passed before the great Soviet geochemist V. I. Vernadsky published his geochemistry book in 1924. Clarke was the first geochemist in the modern sense of the word.

Clarke's book went through five editions, the last of which appeared in 1924. It is now being updated and expanded by the U.S. Geological Survey under the editorship of Michael Fleischer. However, the *Handbook of Geochemistry*, edited by K. H. Wedepohl from 1969 to 1978, is the most complete source of geochemical data currently available.

1.2 Geochemistry in the U.S.S.R.

Geochemistry became an important subject in the U.S.S.R. because of the need to develop the mineral resources of the country. In 1932 Soviet geologists began to analyze systematically collected soil samples using optical spectroscopy (Fersman, 1939). In subsequent years the geologists of the Central Geological and Prospecting Institute in Moscow carried out extensive "metal-lometric" surveys based on soil samples in search of geochemical anomalies.

Geochemistry prospered in the U.S.S.R. because of the popular support it received partly in response to the remarkable work of Alexander Fersman (1883–1945). Fersman studied mineralogy at the University of Moscow under V. I. Vernadsky, who took his students on many field trips and encouraged them to regard minerals as the products of chemical reactions. These were radical departures from conventional mineralogy practiced at the turn of the century. Fersman graduated in 1907 and was elected to a professorship in mineralogy in 1912 at the age of 27. He embarked on an extraordinary career of teaching and research in geochemistry with emphasis on applications. He traveled widely in the U.S.S.R. and explored regions rarely visited before. His sustained interest in the exploration of the Kola Peninsula in the north ultimately led to the discovery of deposits of apatite and nickel ore. As a result, a remote wilderness area was transformed into an important center of mining and industry. Fersman also explored central Asia and discovered a native sulfur deposit at Kara Kum that was actively mined for decades.

Between 1934 and 1939 Fersman published a comprehensive four-volume work entitled *Geochemistry* in which he applied the principles of physical chemistry to the distribution of the chemical elements in nature. Fersman, above all, aroused public interest in geology and geochemistry by his inspiring lectures and popular books. Alexander K. Tolstoy called him a "poet of

stones." Fersman earned this accolade by writing books intended for the layman: *Mineralogy for Everyone* (1928), *Recollections about a Stone* (1940), *My Travels, Stories about Precious Stones*, and *Geochemistry for Everyone* (1958). The last two were published posthumously. Fersman's conviction that geochemistry should serve his country is reflected in his words: "We cannot be merely idle admirers of our vast country; we must actively help reshape it and create a new life" (Shcherbakov, 1958).

The scientific legacy of Fersman's former teacher, Vladimir Ivanovich Vernadsky (1863–1945), is similarly impressive, but it has not been appreciated in the western world. Vernadsky emphasized the importance of the activities of living organisms in geological and geochemical processes. In fact, he regarded living matter as the "most powerful geological force" and wrote that the Earth's crust originated from the biosphere. These convictions about the importance of life on Earth were not widely accepted by geologists in North America, partly because Vernadsky wrote in many languages (Russian, German, French, Czech, Serbo-Croatian, and Japanese). His most important books (Vernadsky, 1924, 1929) were written in French and published in Paris. However, Vernadsky was also far ahead of his contemporaries by concluding that the biosphere may have controlled the environment on the surface of the Earth from the very beginning, long before the existence of life in Early Precambrian time was known (Lapo, 1986). Vernadsky's views on this subject are now reflected in the "Gaia Hypothesis" of Lovelock (1979), made popular on American television in the "Planet Earth" series by the Public Broadcasting System. Vernadsky also identified the biosphere as the principal transformer of solar energy into chemical energy. This idea is now widely accepted. For example, Cloud (1983) described the biosphere as "a huge metabolic device for the capture, storage and transfer of energy." Fossil fuels (coal, oil shale, petroleum, and natural gas) are now regarded as deposits of solar energy collected by the biosphere.

Vernadsky's views on the importance of the biosphere (Vernadsky, 1945) are becoming

increasingly relevant as we attempt to predict the climatic consequences of the "greenhouse effect" caused by the discharge of carbon dioxide and other gases into the atmosphere. We are carrying out an experiment on a global scale the outcome of which could be detrimental to life. The response of the biosphere to this perturbation of the environment may be crucial to the ultimate outcome of this experiment.

V. I. Vernadsky is revered in the U.S.S.R. as one of the giants of science in the 20th century. His teachings still motivate the geochemists working at the Vernadsky Institute of Geochemistry and Analytical Chemistry in Moscow, which is among the foremost geochemical research institutes in the world.

1.3 V. M. Goldschmidt

The Institute of Geochemistry at the University of Göttingen in Germany was made famous by the work of Victor M. Goldschmidt (1888–1947). Goldschmidt earned his doctorate at the University of Oslo in 1911 with a study of contact metamorphism based on the thermodynamic phase rule. In the following year Max von Laue discovered diffraction of x-rays by crystals and thereby provided a method for determining the crystal structure of a mineral and the radii of the ions of which it is composed. From 1922 to 1926 Goldschmidt and his associates at the University of Oslo used x-ray diffraction to determine the crystal structures of many minerals (Goldschmidt, 1930). In 1930 Goldschmidt moved to the University of Göttingen, where he studied the distribution of the chemical elements using an optical spectrograph. From this body of data he deduced that the chemical composition of minerals is determined by the requirements of "closest packing" of ions. Moreover, the substitution of the ions of a major element by the ions of a trace element depends on the similarity of their radii and charges. These generalizations provided a rational explanation for the observed distribution of the elements in the minerals of the crust of the Earth.

Goldschmidt returned to Oslo in 1935 but was unable to continue his work after the

German invasion of Norway in 1940. He fled to Sweden in 1942 and ultimately made his way to England, where he worked at the Macaulay Institute for Soil Research. His health had seriously deteriorated as a consequence of imprisonment in concentration camps in Norway. Goldschmidt returned to Oslo in 1946 but died there prematurely in 1947 at the age of 59. He left behind the manuscript of a partially completed book entitled *Geochemistry*, which was completed by Alex Muir and published posthumously in 1954. A special commemorative issue of *Applied Geochemistry* (1988) was devoted to Goldschmidt on the 100th anniversary of his birthday.

Goldschmidt's principal contribution to geochemistry is the rational explanation of isomorphous substitution in crystals based on the compatibility of the radii and charges of the ions. He thereby achieved one of the major goals of geochemistry. Nevertheless, the urge to know and to understand the distribution of the chemical elements has continued to motivate the work of several outstanding geochemists, notably L. H. Ahrens in South Africa, S. R. Nockolds in England, S. R. Taylor in Australia, K. Rankama in Finland, K. H. Wedepohl in Germany, A. P. Vinogradov in the U.S.S.R., D. M. Shaw in Canada, and K. K. Turekian in the United States.

1.4 Modern Geochemistry

Beginning in the 1950s, geochemists turned increasingly to the study of chemical reactions and processes. The roots of this line of research can be found in the work of A. Fersman, who used the concepts of thermodynamics to study the stability of minerals in their natural environment. In addition, J. H. van't Hoff (1852–1911) studied the crystallization of salts by evaporating seawater in Berlin and, in 1904, the Geophysical Laboratory of the Carnegie Institution of Washington was founded in the United States. The principal objective of the Geophysical Laboratory has been to study the origin of igneous rocks and ore deposits by experimental methods. The results achieved by

N. L. Bowen and his colleagues, and by their successors, at that laboratory have become the foundation of modern igneous petrology. Bowen's book, *The Evolution of the Igneous Rocks*, published in 1928, turned igneous petrology from a preoccupation with the description and classification of igneous rocks toward a concern for their origin and the geochemical differentiation of the Earth by magmatic activity.

In 1952 Brian Mason published the first edition of *Principles of Geochemistry*, which was widely used as a textbook at universities and helped to establish geochemistry as a legitimate component of Earth Science. In the next decade Robert M. Garrels and Konrad B. Krauskopf used thermodynamics and solution chemistry to determine the stability of minerals and the mobility of their ions at the surface of the Earth. They trained the modern generation of geochemists by their own research and through their popular textbooks (Garrels, 1960; Garrels and Christ, 1965; Krauskopf, 1967).

Geochemical prospecting, as we know it today, was initiated in 1947 by the U.S. Geological Survey (Hawkes and Lakin, 1949) and was based on colorimetry. The techniques developed in the United States were used in 1953 for soil surveys in the United Kingdom and in Africa (Webb, 1953). Subsequently, the Geochemical Prospecting Research Center at the Imperial College of Science and Technology in London became a center of activity in this aspect of geochemistry. Geochemical prospecting continues to be one of the most important practical applications of geochemistry and now relies on a wide range of sophisticated analytical techniques.

Environmental geochemistry has arisen recently because of the need to monitor the dispersion of metals and various organic compounds that are introduced into the environment as anthropogenic contaminants. This new application of geochemistry to the welfare of humankind is closely related to pollutant hydrogeology and medical geochemistry. Geochemical prospecting and environmental geochemistry are of paramount importance because they contribute to the continued well-being of the human species on Earth.

Since about the middle of the 20th century geochemistry has become highly diversified into many subdivisions, among them inorganic geochemistry, organic geochemistry, isotope geochemistry, geochemical prospecting, medical geochemistry, aqueous geochemistry, trace-element geochemistry, and cosmochemistry. Each of these subdivisions has its own rapidly growing body of literature. However, the geochemists of the world have organized scientific societies that transcend the boundaries of specialization and help to unify the field. These societies also publish journals that promote the free flow of information and ideas among their members. For example, the Geochemical Society and the Meteoritical Society both sponsor *Geochimica et Cosmochimica Acta*. The European Association for Geochemistry has adopted the journal *Chemical Geology*, and the International Association of Geochemistry and Cosmochemistry sponsors *Applied Geochemistry*. Among other journals that publish papers dealing with geochemistry are

Earth and Planetary Science Letters
Contributions to Mineralogy and Petrology
Journal of Geochemical Exploration
Economic Geology
American Journal of Science
Nature
Science

Some journals are closely associated with certain regions, for example,

<i>Geokhimiya</i>	}	Russia
<i>Doklady (Earth Science Section)</i>		
<i>Lithology and Mineral Resources</i>		
<i>Geochemistry International</i>		
<i>Geochemical Journal</i>		Japan
<i>Chinese Journal of Geochemistry</i>		People's Republic of China

In fact, most Earth Science journals now publish papers in which geochemical data or principles are used to explain a geological process or to solve a particular problem. The strength of geochemistry lies in the fact that most geological processes involve chemical reactions in some significant way. Geochemistry really is for everyone, as Fersman claimed in his popular book.

What then is geochemistry? There is no easy answer to this question because geochemists concern themselves with a wide range of natural phenomena and use many different techniques to study them. According to Fersman, "Geochemistry studies the history of chemical elements in the Earth's crust and their behavior under different thermodynamic and physicochemical natural conditions." Goldschmidt's definition of geochemistry was "Geochemistry is concerned with the laws governing the distribution of the chemical elements and their isotopes throughout the Earth" (Correns, 1969). We could go on and on. Geochemistry is a highly diversified and constantly evolving subject that can be described in many different ways.

For our purposes the major goals of geochemists are

1. To know the distribution of the chemical elements in the Earth and in the solar system.
2. To discover the causes for the observed chemical composition of terrestrial and extraterrestrial materials.
3. To study chemical reactions on the surface of the Earth, in its interior, and in the solar system around us.
4. To assemble this information into geochemical cycles and to learn how these cycles have operated in the geologic past and how they may be altered in the future.

These are the lofty goals of a scientific discipline. Their intrinsic merit is apparent. However, geochemists practicing their craft today also have an obligation to humankind to assist in the devel-

opment and management of natural resources, to monitor the quality of the environment both locally and on a global scale, and to warn humanity against dangerous practices that may threaten the quality of life in the future.

With so much at stake it is not easy to express succinctly what geochemistry is all about. K. O.

Emery and J. M. Hunt (1974, p. 586) put it this way: "Studies of geochemistry ... convert idle speculation into ... understanding ...". That will be the theme of this book. We can no longer afford idle speculation in the Earth Sciences. We must have understanding. Geochemistry can show us how to achieve it.

References

- ASIMOV, I., 1965. *A Short History of Chemistry*. Doubleday, Garden City, NY, 263 pp.
- BOWEN, N. L., 1928. *The Evolution of the Igneous Rocks*. Princeton University Press, Princeton, NJ, 34 pp.
- CLARKE, F. W., 1908. *The Data of Geochemistry*. U.S. Geol. Surv. Bull. 330. (The fifth edition in 1924 is U.S.G.S. Bull. 770.)
- CLOUD, P., 1983. The biosphere. *Sci. Amer.*, **249**:132-144.
- CORRENS, C. W., 1969. The discovery of the chemical elements. The history of geochemistry. Definitions of geochemistry. In K. H. Wedepohl (Ed.), *Handbook of Geochemistry*, vol. 1, 1-11. Springer-Verlag, Berlin, 442 pp.
- EMERY, K. O., and J. M. HUNT, 1974. Summary of Black Sea investigations. In E. T. Degens and D. A. Ross (Eds.), *The Black Sea—geology, chemistry, and biology*, 575-590. *Amer. Assoc. Petrol. Geol., Mem.* 20, 633 pp.
- ERCKER, L., 1951. *Treatise on Ores and Assaying*. From the German Edition of 1580. A Grünhaldt Sisco and C. Stanley Smith, trans. and ann. University of Chicago Press.
- FAUL, H., and C. FAUL, 1983. *It Began with a Stone*. Wiley, New York, 270 pp.
- FERSMAN, A. YE., 1939. Geochemical and mineralogical methods of prospecting. Chapter IV in *Special Methods of Prospecting*. Akad. Nauk S.S.R., Moscow. Translated by L. Hartsock and A. P. Pierce, U.S. Geol. Surv. Circ. 127, 1952.
- FERSMAN, A., 1958. *Geochemistry for Everyone*. Foreign Language Publishing House, Moscow, 454 pp.
- GARRELS, R. M., 1960. *Mineral Equilibria*. Harper & Row, New York.
- GARRELS, R. M., and C. L. CHRIST, 1965. *Solutions, Minerals and Equilibria*. Harper & Row, New York (later Freeman and Cooper, San Francisco), 450 pp.
- GOLDSCHMIDT, V. M., 1930. Geochemische Verteilungsgesetze und kosmische Häufigkeit der Elemente. *Naturwissenschaften*, **18**:999-1013.
- HAWKES, H. E., and H. W. LAKIN, 1949. Vestigial zinc in surface residuum associated with primary zinc ore in east Tennessee. *Econ. Geol.*, **44**:286-295.
- KRAUSKOPF, K. B., 1967. *Introduction to Geochemistry*. McGraw-Hill, New York.
- LAPO, A. V., 1986. V. I. Vernadsky's ideas on the leading role of life in the generation of the Earth's crust. *Earth Sci. Hist.*, **5**:124-127.
- LOVELOCK, J. E., 1979. *Gaia. A New Look at Life on Earth*. Oxford University Press, Oxford, England, 158 pp.
- MASON, B., 1952. *Principles of Geochemistry*. Wiley, New York.
- SHCHERBAKOV, D., 1958. Foreword. In A. Fersman, *Geochemistry for Everyone*. Translated by D. A. Myshne, Foreign Languages Publishing House, Moscow, 453 pp.
- VERNADSKY, V. I., 1924. *La Geochimie*. Alcan, Paris, 404 pp.
- VERNADSKY, V. I., 1929. *La Biosphere*. Alcan, Paris, 232 pp.
- VERNADSKY, V. I., 1945. The biosphere and the noosphere. *Amer. Scientist*, **33**:1-12.
- WEBB, J. S., 1953. A review of American progress in geochemical prospecting. *Inst. Mining Metallurgy Trans.*, **62**:321-348.
- WEDEPOHL, K. H. (Ed.), 1969. *Handbook of Geochemistry*, vol. I. Springer-Verlag, Berlin. Vol. II (1970).

In the Beginning

The urge to trace the history of the universe back to its beginnings is irresistible.

STEVEN WEINBERG (1977, p. 1)

Certain questions about our existence on Earth are so fundamental that they have been incorporated into religious mythologies. These questions not only concern the origin of the Earth and the evolution of life but also extend to the origin of the universe and to the nature of space and time. Did the universe have a beginning and will it ever end? What existed before the universe formed? Does the universe have limits and what exists beyond those limits? It is proper to raise these questions at the beginning of a geochemistry course because they are within the scope of cosmochemistry.

2.1 The Big Bang

The universe started like a bubble in a stream. At first it was not there, and suddenly it formed and expanded rapidly as though it were exploding (Gott, 1982). Science has its share of practical jokers who immediately referred to the start of the expansion of the universe as the Big Bang (Gamow, 1952). From the very beginning the universe had all of the mass and energy it contains today. As a result, its pressure and temperature, say 10^{-32} sec after the Big Bang, were so high that matter existed in its most fundamental form as "quark soup." As the universe expanded and cooled, the quarks combined to form more familiar nuclear particles that ultimately became organized into nuclei of hydrogen and helium.

Formation of atomic nuclei began about 13.8 sec after the Big Bang when the temperature of the universe had decreased to 3×10^9 K. This process continued for about 30 min, but did not go beyond helium because the nuclear reactions could not bridge a gap in the stabilities of the nuclei of lithium, beryllium, and boron. At that time the universe was an intensely hot and rapidly expanding fireball.

Some 700,000 years later, when the temperature had decreased to about 3×10^3 K, electrons became attached to the nuclei of hydrogen and helium. Matter and radiation were thereby separated from each other, and the universe became transparent to light. Subsequently, matter began to be organized into stars, galaxies, and galactic clusters as the universe continued to expand to the present time (Weinberg, 1977).

But how do we know all this? The answer is that the expansion of the universe can be seen in the "red shift" of spectral lines of light emitted by distant galaxies, and it can be "heard" as the "cosmic microwave radiation," which is the remnant of the fireball, that still fills the universe. In addition, the properties of the universe immediately after the Big Bang were similar to those of atomic nuclei. Therefore, a very fruitful collaboration has developed among nuclear physicists and cosmologists that has enabled them to reconstruct the history of the universe back to about 10^{-32} sec after the Big Bang. These studies

have shown that the forces we recognize at low temperature are, at least in part, unified at extremely high temperatures and densities. There is hope that a Grand Unified Theory (GUT) will eventually emerge that may permit us to approach even closer to understanding the start of the universe.

What about the future? Will the universe continue to expand forever? The answer is that the future of the universe can be predicted only if we know the total amount of matter it contains. The matter that is detectable at the present time is not sufficient to permit gravity to overcome the expansion. If expansion continues, the universe will become colder and emptier with no prospect of an end. However, a large fraction of the mass of the universe is hidden from view in the form of gas and dust in interstellar and intergalactic space, and in the bodies of stars that no longer emit light. In addition, we still cannot rule out the possibility that neutrinos have mass even when they are at rest. If the mass of the universe is sufficient to slow the expansion and ultimately to reverse it, then the universe will eventually contract until it disappears again in the stream of time.

Since the universe had a beginning and is still expanding, it cannot be infinite in size. However, the edge of the universe cannot be seen with telescopes because it takes too long for the light to reach us. As the universe expands, space expands with it. In other words, it seems to be impossible to exceed the physical limits of the universe. We are trapped in our expanding bubble. If other universes exist, we cannot communicate with them.

Now that we have seen the big picture, let us review certain events in the history of the standard model of cosmology to show that progress in Science is sometimes accidental.

In 1929 the American astronomer Edwin Hubble reported that eighteen galaxies in the Virgo cluster are receding from Earth at different rates that increase with their distances from Earth. He calculated the recessional velocities of these galaxies by means of the "Doppler effect" from observed increases of the wavelengths of

characteristic spectral lines of light they emit. This "red shift" is related to the recessional velocity by an equation derived in 1842 by Johann Christian Doppler in Prague:

$$\frac{\lambda'}{\lambda} = 1 + \frac{v}{c} \quad (2.1)$$

where λ' is the wavelength of a spectral line of light emitted by a moving source, λ is the wavelength of the same line emitted by a stationary source, c is the velocity of light, and v is the recessional velocity. Hubble's estimates of the distances to the galaxies were based on the properties of the Cepheid Variables studied previously by H. S. Leavitt and H. Shapley at Harvard University. The Cepheid Variables are bright stars in the constellation Cepheus whose period of variation depends on their absolute luminosity, which is the total radiant energy emitted by an astronomical body. Hubble found such variable stars in the galaxies he was studying and determined their absolute luminosities from their periods. The intensity of light emitted by a star decreases as the square of the distance increases. Therefore, the distance to a star can be determined from a comparison of its absolute and its apparent luminosity, where the latter is defined as the radiant power received by the telescope per square centimeter. In this way, Hubble determined the recessional velocities and distances of the galaxies in the Virgo cluster and expressed their relationship as:

$$v = Hd \quad (2.2)$$

where v is the recessional velocity in km/sec, d is the distance in 10^6 light years, and H is the Hubble constant (Hubble, 1936).

The Hubble constant can be used to place a limit on the age of the universe. If two objects are moving apart with velocity v , the time (t) required for them to become separated by a distance d is:

$$t = \frac{d}{v} = \frac{1}{H} \quad (2.3)$$

The initial results indicated that the Hubble constant had a value of 170 km/sec/ 10^6 light years,

which corresponds to an expansion time of less than 2×10^9 years. This result was very awkward because age determinations based on radioactivity had established that the Earth is older than this date. Eventually Walter Baade discovered an error in the calibration of the Cepheid Variables, and the value of the Hubble constant was revised (Baade, 1968). The presently accepted value is 15 km/sec/ 10^6 light years, which indicates an expansion time for the universe of less than 20×10^9 years. This date is compatible with independent estimates of its age based on consideration of nucleosynthesis and the evolution of stars. By combining all three methods Hainebach et al. (1978) refined the age of the universe to $(14.5 \pm 1.0) \times 10^9$ years.

The Big Bang theory of cosmology was not accepted for many years for a variety of reasons. The turning point came in 1964 when Arno A. Penzias and Robert W. Wilson discovered a microwave background radiation that corresponds to a blackbody temperature of about 3 K. The discovery of this radiation was accidental, even though its existence had been predicted twenty years earlier by George Gamow and his colleagues Ralph A. Alpher and Robert Herman. Because they were unaware of Gamow's work, Penzias and Wilson were skeptical about the phenomenon they had discovered and took great care to eliminate all extraneous sources of the background radiation. For example, they noticed that two pigeons had been nesting in the throat of the antenna they were using at Holmdel, New Jersey. The pigeons were caught and taken to a distant location, but promptly returned. Therefore, they were caught again and dealt with "by more decisive means." The pigeons had also coated the antenna with a "white dielectric material," which was carefully removed. However, the intensity of the background radiation remained constant and independent of time in the course of a year.

Word of this phenomenon reached a group of astrophysicists at nearby Princeton University who were working on models of the early history of the universe under the guidance of Robert H. Dicke. Eventually, Penzias called Dicke, and it

was agreed that they would publish two companion letters in the *Astrophysical Journal*. Penzias and Wilson announced the discovery, and Dicke and his colleagues explained the cosmological significance of the microwave background radiation (Penzias and Wilson, 1965). In 1978 Penzias and Wilson shared the Nobel Prize in physics for their discovery.

The radiation discovered by Penzias and Wilson is a remnant of the radiation that filled the universe for about 700,000 years when its temperature was greater than about 3000 K. During this early period, matter consisted of a mixture of nuclear particles and photons in thermal equilibrium with each other. Under these conditions the energy of radiation at a specific wavelength is inversely proportional to the absolute temperature. According to an equation derived by Max Planck at the start of the 20th century, the energy of blackbody radiation at a particular temperature increases rapidly with increasing wavelength to a maximum and then decreases at longer wavelengths. Radiation in thermal equilibrium with matter has the same properties as radiation inside a black box with opaque walls. Therefore, the energy distribution of radiation in the early universe is related to the wavelength and to the absolute temperature by Planck's equation. The wavelength near which most of the energy of blackbody radiation is concentrated ($\lambda_{\max}$) is approximately equal to:

$$\lambda_{\max} = \frac{0.29}{T} \quad (2.4)$$

where $\lambda_{\max}$ is measured in centimeters and T is in Kelvins (Weinberg, 1977).

The original measurement of Penzias and Wilson was at a wavelength of 7.35 cm, which is much greater than the typical wavelength of radiation at 3 K. Since 1965, many additional measurements at different wavelengths have confirmed that the cosmic background radiation does fit Planck's formula for blackbody radiation. The characteristic temperature of this radiation is about 3 K, indicating that the typical wavelength of photons has increased by a factor of about 1000

because of the expansion of the universe since its temperature was 3000 K (Weinberg, 1977).

2.2 Stellar Evolution

Matter in the universe is organized into a "hierarchy of heavenly bodies" listed below in order of decreasing size.

clusters of galaxies	comets
galaxies	asteroids
stars, pulsars, and black holes	meteoroids
planets	dust particles
satellites	molecules
	atoms of H and He

On a subatomic scale, space between stars and galaxies is filled with cosmic rays (energetic nuclear particles) and photons (light).

Stars are the basic units in the hierarchy of heavenly bodies within which matter continues to evolve by nuclear reactions. Many billions of stars are grouped together to form a galaxy, and large numbers of such galaxies are associated into galactic clusters. Stars may have stellar companions or they may have orbiting planets, including ghostly comets that flare briefly when they approach the star on their eccentric orbits. The planets in our solar system have their own retinue of satellites. The space between Mars and Jupiter contains the asteroids, most of which are fragments of larger bodies that have been broken up by collisions and by the gravitational forces of Jupiter and Mars. Pieces of the asteroids have impacted as meteorites on the surfaces of the planets and their satellites and have left a record of these events in craters.

On an even smaller scale, space between stars contains clouds of gas and solid particles. The gas is composed primarily of hydrogen and of helium that were produced during the initial expansion of the universe. In addition, the interstellar medium contains elements of higher atomic number that were synthesized by nuclear reactions in the interiors of stars that have since exploded. A third component consists of compounds of hydrogen and carbon that are the precursors of life. These

clouds of gas and dust may contract to form new stars whose evolution depends on their masses and on the H/He ratio of the gas cloud from which they formed.

The evolution of stars can be described by specifying their luminosities and surface temperatures. The luminosity of a star is proportional to its mass, and its surface temperature or color is an indicator of its volume. When a cloud of interstellar gas contracts, its temperature increases, and it begins to radiate energy in the infrared and visible parts of the spectrum. As the temperature in the core of the gas cloud approaches 20×10^6 K, energy production by hydrogen fusion becomes possible, and a star is born. Most of the stars of a typical galaxy derive energy from this process and therefore plot in a band, called the *main sequence*, on the Hertzsprung–Russell diagram shown in Figure 2.1. Massive stars, called *blue giants*, have high luminosities and high surface temperatures. The Sun is a star of intermediate mass and has a surface temperature of about 5800 K. Stars that are less massive than the Sun are called *red dwarfs* and plot at the lower end of the main sequence.

As a star five times more massive than the Sun converts hydrogen to helium while on the main sequence, the density of the core increases, causing the interior of the star to contract. The core temperature therefore rises slowly during the hydrogen-burning phase. This higher temperature accelerates the fusion reaction and causes the outer envelope of the star to expand. However, when the core becomes depleted in hydrogen, the rate of energy production declines and the star contracts, raising the core temperature still further. The site of energy production now shifts from the core to the surrounding shell. The resulting changes in luminosity and surface temperature cause the star to move off the main sequence toward the realm of the *red giants* (Figure 2.1).

The helium produced by hydrogen fusion in the shell accumulates in the core, which continues to contract and therefore gets still hotter. The resulting expansion of the envelope lowers the surface temperature and causes the color to turn red. At the same time, the shell in which hydrogen

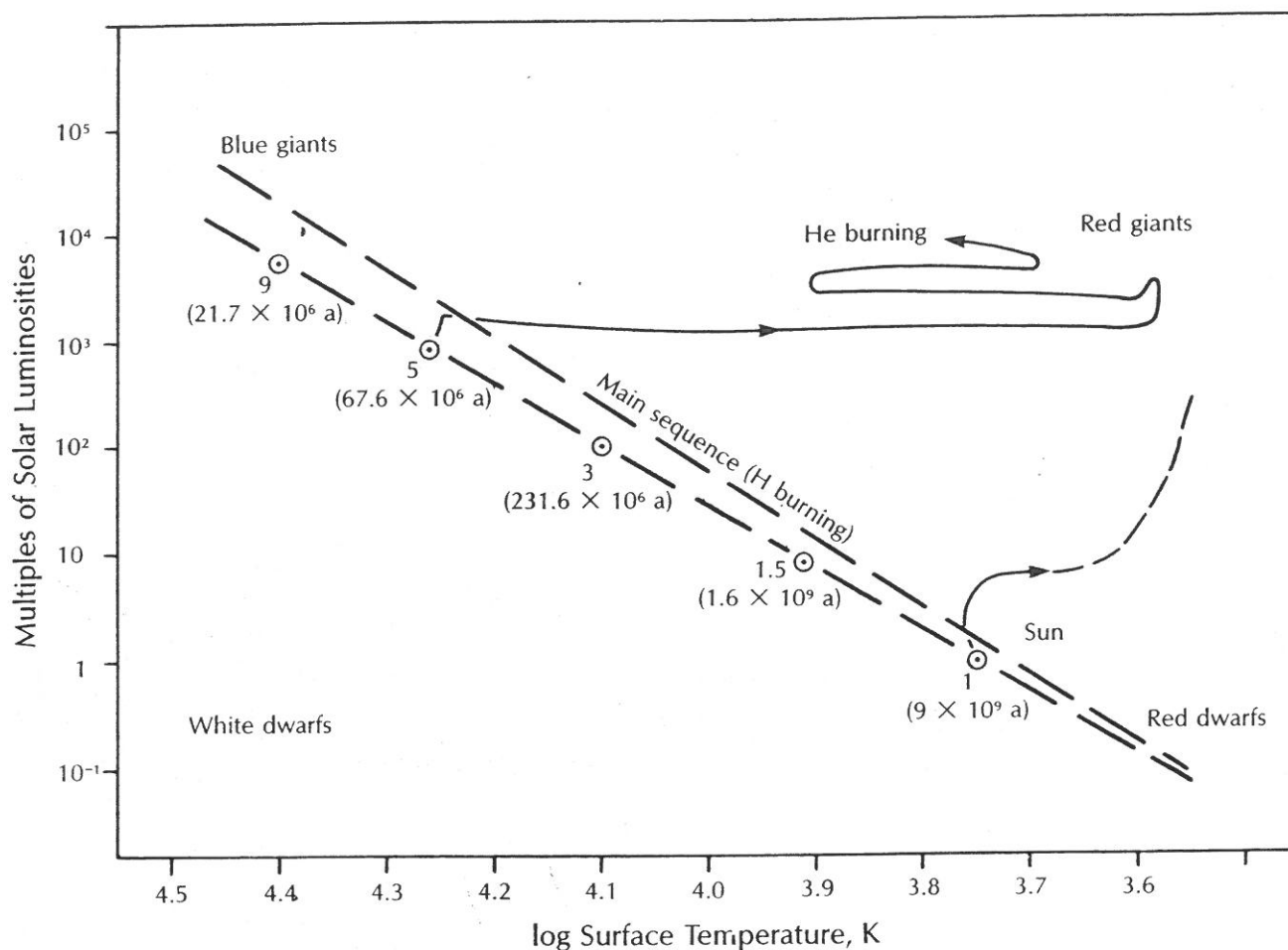


Figure 2.1 Stellar evolution on a Hertzsprung–Russell diagram for stars ranging from 1 to 9 solar masses.

When a star has used up the hydrogen in its core, it contracts and then moves off the main sequence and enters the realm of the red giants, which generate energy by helium fusion. The evolutionary track and the life expectancy of stars are strongly dependent on their masses. Stars five times more massive than the sun are nearly 1000 times brighter, have surface temperatures of about 18,000 K—compared to 5800 K for the Sun—and remain on the main sequence only about 68 million years. Their evolution to the end of the major phase of helium burning takes only about 87 million years (Iben, 1967).

is reacting gradually thins as it moves toward the surface, and the luminosity of the star declines. These changes transform a main-sequence star into a bloated red giant. For example, the radius of a star five times more massive than the Sun increases about 30-fold just before helium burning in the core begins.

When the core temperature approaches 100×10^6 K, helium fusion by means of the “triple-alpha process” begins and converts three helium nuclei into the nucleus of carbon-12. At the same

time, hydrogen fusion in the shell around the core continues. The luminosities and surface temperatures (color) of red giants become increasingly variable as they evolve, reflecting changes in the rates of energy production in the core and shell. The evolutionary tracks in Figure 2.1 illustrate the importance of the mass of a star to its evolution. A star five times as massive as the Sun is 1000 times brighter while on the main sequence and has a more eventful life as a red giant than stars below about two solar masses (Iben, 1967, 1974).

The length of time a star spends on the main sequence depends primarily on its mass and to a lesser extent on the H/He ratio of its ancestral gas cloud. In general, massive stars (blue giants) consume their fuel rapidly and may spend only 10×10^6 years on the main sequence. Small stars (red dwarfs) have much slower "metabolic" rates and remain on the main sequence for very long periods of time exceeding 10×10^9 years. The Sun, being a star of modest magnitude, has enough hydrogen in its core to last about 9×10^9 years at the present rate of consumption. Since it formed about 4.5×10^9 years ago, the Sun has achieved middle age and will provide energy to the planets of the solar system for a very long time to come. However, ultimately its luminosity will increase, and it will expand to become a red giant, as shown in Figure 2.1. The temperature on the surface of the Earth will then rise and become intolerable to life forms. The expansion of the Sun may engulf the terrestrial planets, including Earth, and vaporize them. When all of its nuclear fuel has been consumed, the Sun will assume the end stage of stellar evolution that is appropriate for a star of its mass and chemical composition.

Toward the end of the giant stage, stars become increasingly unstable. When the fuel for a particular energy-producing reaction is exhausted, the star contracts and its internal temperature rises. The increase in temperature may trigger a new set of nuclear reactions. In stars of sufficient mass, this activity culminates in a gigantic explosion (supernova) as a result of which a large fraction of the outer envelope of the star is blown away. The debris from such explosions mixes with hydrogen and helium in interstellar space to form clouds of gas and dust from which new stars may form.

As stars reach the end of their evolution they turn into white dwarfs, or neutron stars (pulsars), or black holes, depending on their masses (Wheeler, 1973). Stars whose mass is less than about 1.2 solar masses contract until their radius is only about 1×10^4 km and their density is between 10^4 and 10^8 g/cm³. Stars in this configuration have low luminosities but high surface temperatures and are therefore called white dwarfs (Figure 2.1). They gradually cool and fade from

view as their luminosities and surface temperatures diminish with time. Stars that are appreciably more massive than the Sun develop dense cores because of the synthesis of heavy chemical elements by nuclear reactions. Eventually, such stars become unstable and explode as supernovas. The core then collapses until its radius is reduced to about 10 km and its density is of the order of 10^{11} to 10^{15} g/cm³. Such stars are composed of a "neutron gas" because electrons and protons are forced to combine under the enormous pressure and the abundance of neutrons greatly increases as a result. Neutron stars have very rapid rates of rotation and emit pulsed radio waves that were first observed in 1965 by Jocelyn Bell, a graduate student working with A. Hewish at the Cavendish Laboratory of Cambridge University in England (Hewish, 1975). The Crab Nebula contains such a "pulsar," which is the remnant of a supernova observed by Chinese astronomers in 1054 A.D. (Fowler, 1967). The cores of the most massive stars collapse to form black holes in accordance with Einstein's theory of general relativity. Black holes have radii of only a few kilometers and densities in excess of 10^{16} g/cm³. Their gravitational field is so great that neither light nor matter can escape from them, hence the name "black hole." Observational evidence supporting the existence of black holes is growing and they are believed to be an important phenomenon in the evolution of galaxies.

Stars, it seems, have predictable evolutionary life cycles. They form, shine brightly for a while, and then die. Hans Bethe (1968, p. 547) put it this way:

If all this is true, stars have a life cycle much like animals. They are born, they grow, they go through a definite internal development, and finally die, to give back the material of which they are made so that new stars may live.

2.3 Nucleosynthesis

The origin of the chemical elements is intimately linked to the evolution of stars because the elements are synthesized by the nuclear reactions from which stars derive the energy they radiate into space. Only helium and deuterium, the

heavy isotope of hydrogen, were synthesized during the initial expansion of the universe. The entire theory of nucleosynthesis was presented in a detailed paper by Burbidge, Burbidge, Fowler and Hoyle (1957) referred to affectionately as B₂FH. Subsequent contributions (e.g., Schramm and Arnett, 1973) have been concerned with specific aspects of the theory and its application to the evolution of stars of different masses and initial compositions.

The theory presented by B₂FH (1957) evolved from the work of several other scientists, among whom George Gamow deserves special recognition. Gamow received his doctorate from the University of Leningrad and came to the University of Göttingen in the spring of 1928 for some postdoctoral studies. There he met Fritz Houtermans, with whom he spent many hours in a café making calculations (Gamow, 1963). Subsequently, Houtermans moved to the University of Berlin where he met the British astronomer Robert Atkinson. Houtermans and Atkinson used Gamow's theory of alpha decay to propose that stars generate energy in their interiors by the formation of helium nuclei from four protons captured by the nucleus of another light element. The initial title of their paper was "Wie kann man einen Heliumkern im Potentialtopf kochen." (How one can cook a helium nucleus in a pressure cooker.) Needless to say, the editors of the *Zeitschrift für Physik* insisted that the title be changed (Atkinson and Houtermans, 1929).

Ten years later, in April of 1938, Gamow organized a conference in Washington, D.C., to discuss the internal constitution of stars. The conference stimulated one attendee, Hans Bethe, to examine the possible nuclear reactions between protons and the nuclei of the light elements in order of increasing atomic number. Bethe (1939) found that the "pressure cooker" of Atkinson and Houtermans was the nucleus of $^{12}_6\text{C}$ and made it the basis of his famous CNO cycle for hydrogen fusion in stars (to be presented later in this section) (Bethe, 1968).

Gamow influenced the evolution of the theory of nucleosynthesis in many other ways. In 1935 he published a paper in the *Ohio Journal of*

Science (an unlikely place for a nuclear astrophysics paper) on the buildup of heavy elements by neutron capture and subsequently championed the idea that the chemical elements were synthesized during the first 30 min after the Big Bang. In the mid-1940s Alpher and Gamow wrote a paper detailing the origin of the chemical elements based on that assumption. At Gamow's suggestion, Hans Bethe's name was added "in absentia," thus creating the famous triumvirate Alpher, Bethe, and Gamow (1948).

The abundance of the chemical elements and their naturally occurring isotopes is the blueprint for all theories of nucleosynthesis. For this reason, geochemists and stellar spectroscopists have devoted much time and effort to obtaining accurate analytical data on the concentrations of the elements in the Sun and other nearby stars from the wavelength spectra of the light they emit. Information on the abundances of nonvolatile elements has come also from chemical analyses of stony meteorites, especially the carbonaceous chondrites, which are the most undifferentiated samples of matter in the solar system available to us (Mason, 1962). Table 2.1 lists the abundances of the elements in the solar system compiled by Anders and Ebihara (1982). The abundances are expressed in terms of the number of atoms relative to 10^6 atoms of silicon. Figure 2.2 is a plot of these data and illustrates several important observations about the abundances of the elements.

1. Hydrogen and helium are by far the most abundant elements in the solar system, and the atomic H/He ratio is about 12.5.
2. The abundances of the first 50 elements decrease exponentially.
3. The abundances of the elements having atomic numbers greater than 50 are very low and do not vary appreciably with increasing atomic number.
4. Elements having even atomic numbers are more abundant than their immediate neighbors with odd atomic numbers (Oddo-Harkins rule).

Table 2.1 Abundances of the Elements in the Solar System in Units of Number of Atoms per 10^6 Atoms of Silicon

Atomic no.	Element	Symbol	Abundance ^a	Atomic no.	Element	Symbol	Abundance ^a
1	hydrogen	H	2.72×10^{10}	53	iodine	I	9.0×10^{-1}
2	helium	He	2.18×10^9	54	xenon	Xe	4.35×10^0
3	lithium	Li	5.97×10^1	55	cesium	Cs	3.72×10^{-1}
4	beryllium	Be	7.8×10^{-1}	56	barium	Ba	4.36×10^0
5	boron	B	2.4×10^1	57	lanthanum	La	4.48×10^{-1}
6	carbon	C	1.21×10^7	58	cerium	Ce	1.16×10^0
7	nitrogen	N	2.48×10^6	59	praseodymium	Pr	1.74×10^{-1}
8	oxygen	O	2.01×10^7	60	neodymium	Nd	8.36×10^{-1}
9	fluorine	F	8.43×10^2	61	promethium	Pm	0
10	neon	Ne	3.76×10^6	62	samarium	Sm	2.61×10^{-1}
11	sodium	Na	5.70×10^4	63	europium	Eu	9.72×10^{-2}
12	magnesium	Mg	1.075×10^6	64	gadolinium	Gd	3.31×10^{-1}
13	aluminum	Al	8.49×10^4	65	terbium	Tb	5.89×10^{-2}
14	silicon	Si	1.00×10^6	66	dysprosium	Dy	3.98×10^{-1}
15	phosphorus	P	1.04×10^4	67	holmium	Ho	8.75×10^{-2}
16	sulfur	S	5.15×10^5	68	erbium	Er	2.53×10^{-1}
17	chlorine	Cl	5.240×10^3	69	thulium	Tm	3.86×10^{-2}
18	argon	Ar	1.04×10^5	70	ytterbium	Yb	2.43×10^{-1}
19	potassium	K	3.770×10^3	71	lutetium	Lu	3.69×10^{-2}
20	calcium	Ca	6.11×10^4	72	hafnium	Hf	1.76×10^{-1}
21	scandium	Sc	3.38×10^1	73	tantalum	Ta	2.26×10^{-2}
22	titanium	Ti	2.400×10^3	74	tungsten	W	1.37×10^{-1}
23	vanadium	V	2.95×10^2	75	rhenium	Re	5.07×10^{-2}
24	chromium	Cr	1.34×10^4	76	osmium	Os	7.17×10^{-1}
25	manganese	Mn	9.510×10^3	77	iridium	Ir	6.60×10^{-1}
26	iron	Fe	9.00×10^5	78	platinum	Pt	1.37×10^0
27	cobalt	Co	2.250×10^3	79	gold	Au	1.86×10^{-1}
28	nickel	Ni	4.93×10^4	80	mercury	Hg	5.2×10^{-1}
29	copper	Cu	5.14×10^2	81	thallium	Tl	1.84×10^{-1}
30	zinc	Zn	1.260×10^3	82	lead	Pb	3.15×10^0
31	gallium	Ga	3.78×10^2	83	bismuth	Bi	1.44×10^{-1}
32	germanium	Ge	1.18×10^2	84	polonium	Po	~0
33	arsenic	As	6.79×10^0	85	astatine	At	~0
34	selenium	Se	6.21×10^1	86	radon	Rn	~0
35	bromine	Br	1.18×10^1	87	francium	Fr	~0
36	krypton	Kr	4.53×10^1	88	radium	Ra	~0
37	rubidium	Rb	7.09×10^0	89	actinium	Ac	~0
38	strontium	Sr	2.38×10^1	90	thorium	Th	3.35×10^{-2}
39	yttrium	Y	4.64×10^0	91	protactinium	Pa	~0
40	zirconium	Zr	1.07×10^1	92	uranium	U	9.00×10^{-3}
41	niobium	Nb	7.1×10^{-1}	93	neptunium	Np	~0
42	molybdenum	Mo	2.52×10^0	94	plutonium	Pu	~0
43	technetium	Tc	0	95	americium	Am	0
44	ruthenium	Ru	1.86×10^0	96	curium	Cm	0
45	rhodium	Rh	3.44×10^{-1}	97	berkelium	Bk	0
46	palladium	Pd	1.39×10^0	98	californium	Cf	0
47	silver	Ag	5.29×10^{-1}	99	einsteinium	Es	0
48	cadmium	Cd	1.69×10^0	100	fermium	Fm	0
49	indium	In	1.84×10^{-1}	101	mendelevium	Md	0
50	tin	Sn	3.82×10^0	102	nobelium	No	0
51	antimony	Sb	3.52×10^{-1}	103	lawrencium	Lr	0
52	tellurium	Te	4.91×10^0				

^aThe terrestrial abundances of the radioactive daughters of uranium and thorium are very low and are therefore indicated as “~0.” In addition, neptunium and plutonium are produced in nuclear reactors and therefore occur on the Earth. However, the transuranium elements having atomic numbers of 95 or greater do not occur in the solar system. Their abundances are therefore stated as “0.” SOURCE: Anders and Ebihara (1982).

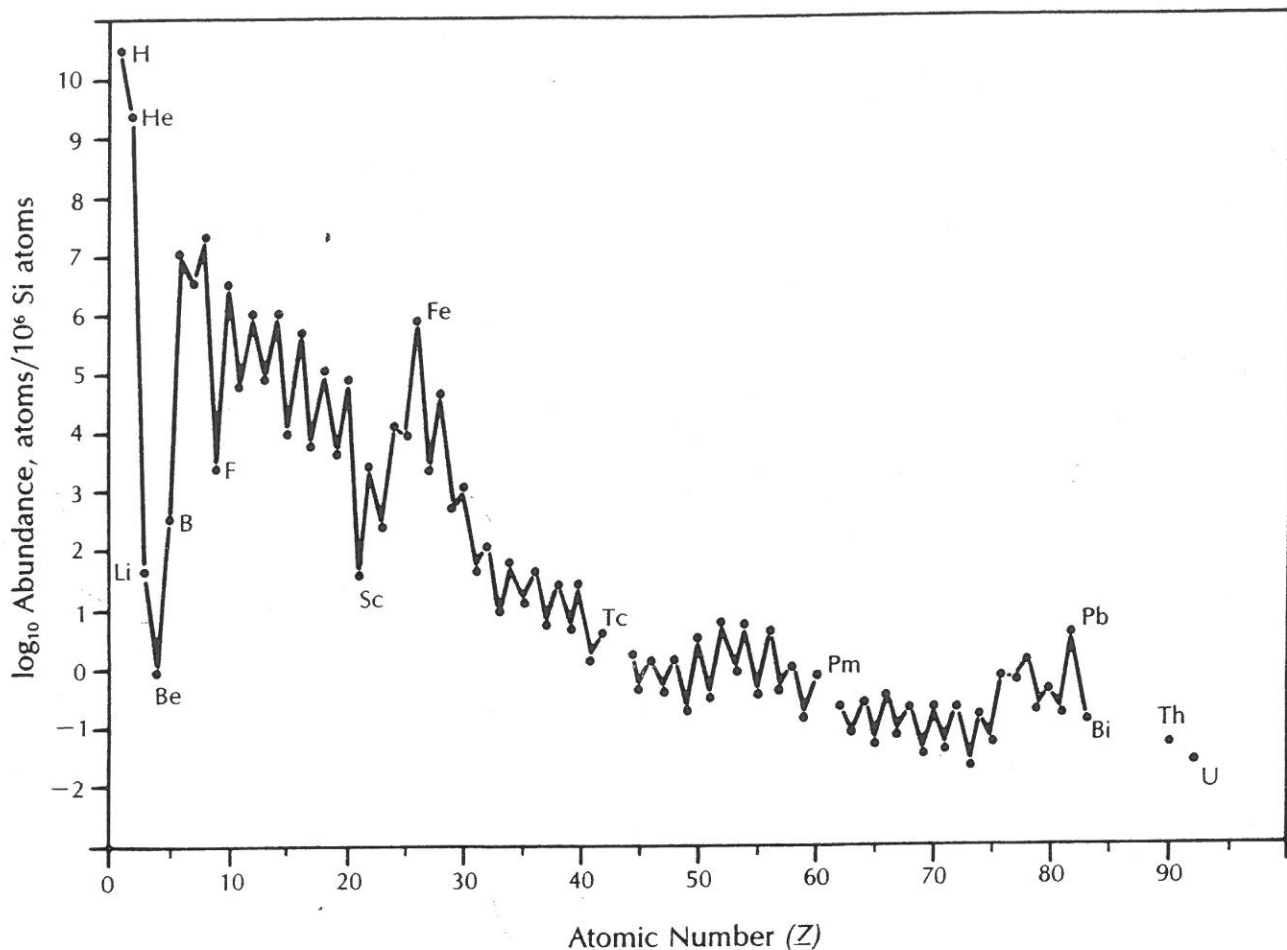


Figure 2.2 Abundances of the chemical elements in the solar system in terms of atoms per 10^6 atoms of Si. The data were derived primarily by analysis of carbonaceous chondrite meteorites and by optical spectroscopy of light from the Sun and nearby stars (Anders and Ebihara, 1982).

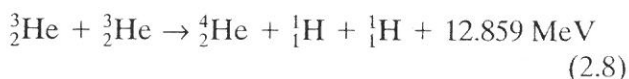
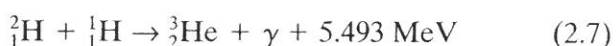
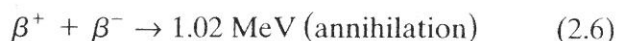
5. The abundances of lithium, beryllium, and boron are anomalously low compared to other elements of low atomic number.
6. The abundance of iron is notably higher than those of other elements with similar atomic numbers.
7. Two elements, technetium and promethium, do not occur in the solar system because all of their isotopes are unstable and decay rapidly.
8. The elements having atomic numbers greater than 83 (Bi) have no stable isotopes, but occur naturally at very low abundances because they are the daugh-

ters of long-lived radioactive isotopes of uranium and thorium.

The nucleosynthesis model of B₂FH (1957) includes eight different kinds of nuclear reactions that occur at specified temperatures in the course of the evolution of a star. Several of these reactions may take place simultaneously in the cores and outer shells of massive stars. As a result, the core of a star may have a different chemical composition than the shell surrounding it. Moreover, not all of the nuclear processes take place in all stars. Consequently, other stars in the Milky Way Galaxy do not necessarily have the same chemical composition as the Sun and her planets.

All stars on the main sequence generate energy by hydrogen fusion reactions. This process results in the synthesis of helium either by the direct proton-proton chain (equations 2.5–2.8) or by the CNO cycle (equations 2.9–2.14). The proton-proton chain works as follows. Two nuclei of hydrogen, consisting of one proton each, collide to form the nucleus of deuterium (${}^2_1\text{H}$) plus a positron (β^+) and a neutrino (ν). (The designation of atomic species is presented in Chapter 6.) Each reaction of this kind liberates 0.422 million electron volts (MeV) of energy. The positron (positively charged electron) is annihilated by interacting with a negatively charged electron giving off additional energy of 1.02 MeV. The deuterium nucleus collides with another proton to form the nucleus of helium-3 (${}^3_2\text{He}$) plus a gamma ray (γ) and 5.493 MeV of energy. Finally, two helium-3 nuclei must collide to form helium-4 (${}^4_2\text{He}$), two protons, and 12.859 MeV. The end result is that four hydrogen nuclei fuse to form one nucleus of helium-4, a gamma ray, a neutrino, and 19.794 MeV of energy.

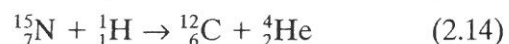
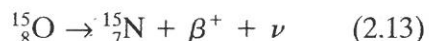
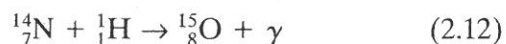
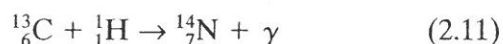
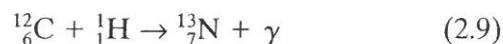
The entire process can be described by a series of equations in which the nuclei of hydrogen and helium are represented by the symbols of the appropriate isotopes (see Chapter 6), even though these isotopes do not actually exist in atomic form in stellar interiors where their electrons are removed from them because of the high temperature:



The direct proton-proton fusion to form helium-4 can only take place at a temperature of about 10×10^6 K, and even then the probability of its occurrence (or its “reaction cross section”) is very small. Nevertheless, this process was the only source of nuclear energy for first-generation stars that formed from the primordial mixture of hydrogen and helium after the Big Bang.

Once the first generation of stars had run through their evolutionary cycles and had exploded,

the interstellar gas clouds contained elements of higher atomic number. The presence of carbon-12 (${}^{12}_6\text{C}$) synthesized by the ancestral stars has made it easier for subsequent generations of stars to generate energy by hydrogen fusion. This alternative mode of hydrogen fusion was discovered by Hans Bethe and is known as the CNO cycle:



The end result is that four protons are fused to form one nucleus of ${}^4_2\text{He}$, as in the direct proton-proton chain. The nucleus of ${}^{12}_6\text{C}$ acts as a sort of catalyst and is released at the end. It can then be reused for another revolution of the CNO cycle.

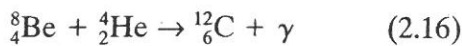
The Sun contains elements of higher atomic number than helium including ${}^{12}_6\text{C}$ and therefore carries on hydrogen fusion by the CNO cycle. In fact, most stars in our Milky Way Galaxy are second-generation stars because our Galaxy is so old that only the very smallest first-generation stars could have survived to the present time.

The low reaction cross section of the proton-proton chain by which the ancestral stars generated energy has been a source of concern to nuclear astrophysicists. When this difficulty was pointed out to Sir Arthur Eddington, who proposed hydrogen fusion in stars in 1920, he replied (Fowler, 1967):

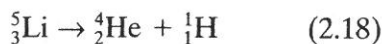
We do not argue with the critic who urges that the stars are not hot enough for this process; we tell him to go and find a hotter place.

After the hydrogen in the core has been converted to helium “ash,” hydrogen fusion ends, and the core contracts under the influence of gravity. The core temperature rises toward 100×10^6 K, and the helium “ash” becomes the fuel for the next set of energy-producing nuclear reactions. The critical reaction for helium burning is the fusion of three

alpha particles (triple-alpha process) to form a nucleus of $^{12}_6\text{C}$:

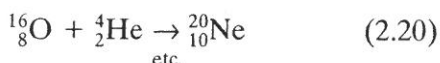
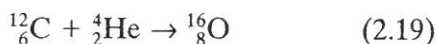


This is the critical link in the chain of nucleosynthesis because it bridges the gap in nuclear stability of the isotopes of lithium, beryllium, and boron. The crux of the problem is that the nucleus of ^8_4Be is very unstable and decays quickly with a "half-life" of about 10^{-16} sec. Therefore, ^8_4Be must absorb a third helium nucleus very soon after its formation to make it safely to stable $^{12}_6\text{C}$ (Fowler, 1967). An alternative reaction involving the addition of a proton to the nucleus of ^4_2He has an even smaller chance to succeed because the product, ^5_3Li , has a half-life of only 10^{-21} sec and decomposes to form helium and hydrogen:



The triple-alpha process is indeed the key to the synthesis of all elements beyond helium. Without it, stellar evolution would be short-circuited, and the universe would be composed only of hydrogen and helium.

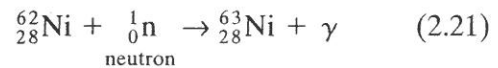
Helium burning sustains red giants only for a few tens of millions of years or less. With increasing temperature in the core, alpha particles fuse with the nuclei of $^{12}_6\text{C}$ to produce nuclei of still higher atomic number:



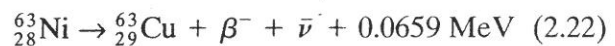
However, electrostatic repulsion between positively charged nuclei and alpha particles limits the size of the atoms that can form in this way. The heaviest atom produced by the addition of alpha particles is $^{56}_{28}\text{Ni}$, which decays to $^{56}_{27}\text{Co}$ and then to stable $^{56}_{26}\text{Fe}$. These nuclear reactions therefore cause the enhanced abundance of the elements in the iron group illustrated in Figure 2.2.

During the final stages of the evolution of red giants, several other kinds of nuclear reactions occur (B₂FH, 1957). The most important of these

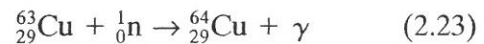
are the neutron-capture reactions, which produce a large number of the atoms having atomic numbers greater than 26 (Fe). These reactions involve the addition of a neutron to the nucleus of an atom to produce an isotope having the same atomic number but a large mass number. For example, the equation:



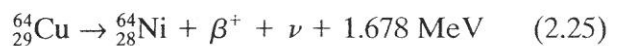
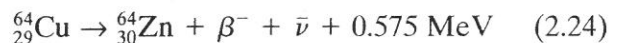
indicates that the nucleus of $^{62}_{28}\text{Ni}$ absorbs a neutron, which changes it to an excited state of $^{63}_{28}\text{Ni}$, which then deexcites by emitting a gamma ray. Nickel-63 is radioactive and decays to stable $^{63}_{29}\text{Cu}$ by emitting a β^- particle:



where $\bar{\nu}$ is an antineutrino. $^{63}_{29}\text{Cu}$ is a stable isotope of copper and can absorb another neutron to form $^{64}_{29}\text{Cu}$:

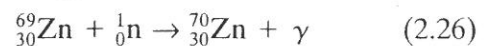


Copper-64 is radioactive and undergoes branched decay to form $^{64}_{30}\text{Zn}$ and $^{64}_{28}\text{Ni}$, both of which are stable:



This process of successive additions of neutrons is illustrated in Figure 2.3. It takes place during the red giant stage of stellar evolution when the neutron flux is low enough to permit the product nucleus to decay before the next neutron is added. This process therefore is characteristically *slow* and is therefore referred to as the *s-process*.

By examining Figure 2.3 closely we see that the track of the s-process bypasses $^{70}_{30}\text{Zn}$, which is one of the stable isotopes of zinc. In order to make this isotope by neutron capture reactions, the pace must be speeded up so that unstable $^{69}_{30}\text{Zn}$ can pick up a neutron to form $^{70}_{30}\text{Zn}$ before it decays to stable $^{70}_{31}\text{Ga}$:



An even more rapid rate of neutron capture is required to make $^{70}_{30}\text{Zn}$ from $^{65}_{29}\text{Cu}$ by addition of five neutrons in succession to form $^{70}_{29}\text{Cu}$, which then decays by β^- emission to stable $^{70}_{30}\text{Zn}$:

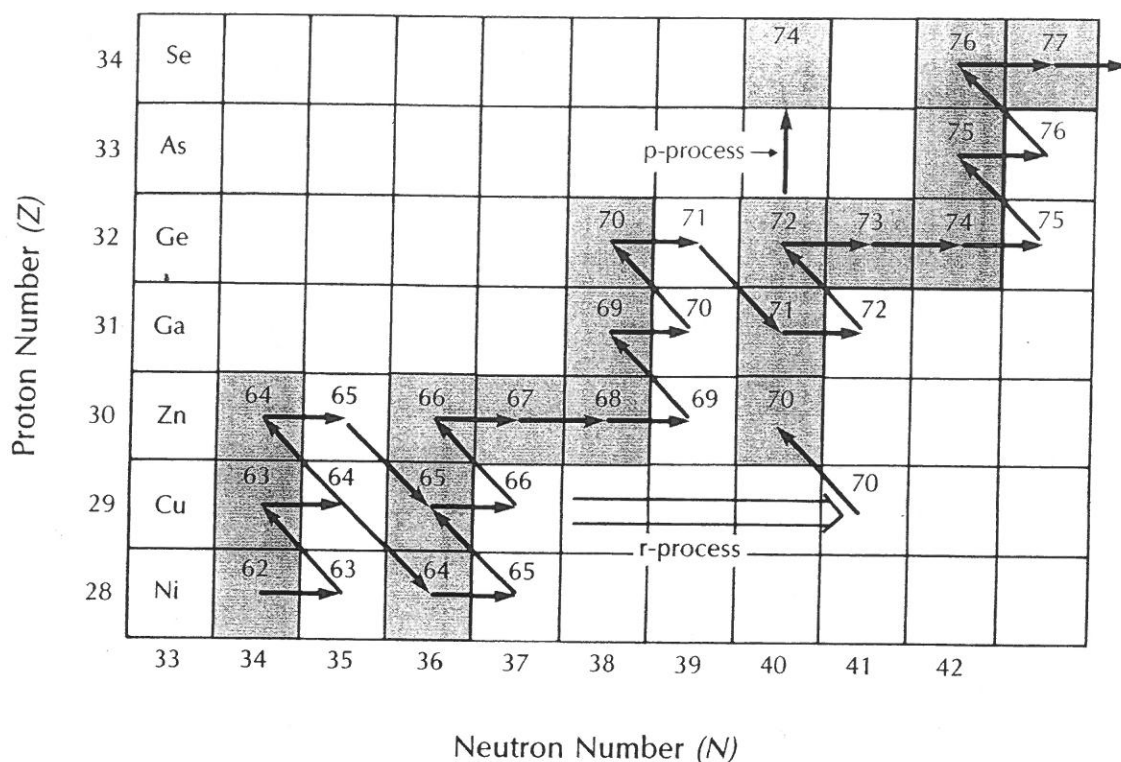
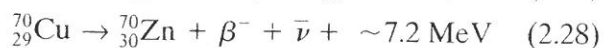
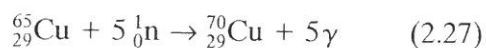
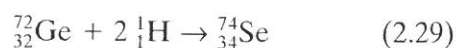


Figure 2.3 Nucleosynthesis in red giants by neutron capture on a slow time scale (*s*-process) followed by beta decay. The dark squares are stable isotopes, whereas the unshaded ones are radioactive. The process starts with stable $^{62}_{28}\text{Ni}$, which absorbs a neutron to form unstable $^{63}_{28}\text{Ni}$, which decays to stable $^{63}_{29}\text{Cu}$ by emitting a β^- particle. The main line of the *s*-process, as indicated by arrows, proceeds from $^{62}_{28}\text{Ni}$ to $^{77}_{34}\text{Se}$ and beyond but bypasses $^{70}_{30}\text{Zn}$ and $^{74}_{34}\text{Se}$. $^{70}_{30}\text{Zn}$ is produced by neutron capture on a rapid time scale (*r*-process) from $^{68}_{30}\text{Zn}$ via unstable $^{69}_{30}\text{Zn}$ and from $^{65}_{29}\text{Cu}$, which captures five neutrons in rapid succession to form $^{70}_{30}\text{Cu}$ followed by decay to stable $^{70}_{30}\text{Zn}$. $^{74}_{34}\text{Se}$ is a proton-rich nuclide that cannot form by either the *s*-process or the *r*-process and requires the addition of two protons (*p*-process) to stable $^{72}_{32}\text{Ge}$.



Capture of neutrons at such *rapid* rates is characteristic of the *r*-process, which requires a much greater neutron flux than the *s*-process and therefore takes place only during the last few minutes in the life of a red giant when it explodes as a supernova.

However, no neutron capture on any time scale can account for the formation of some atoms such as stable $^{74}_{34}\text{Se}$ shown also in Figure 2.3. This nuclide is synthesized by the addition of two protons to stable $^{72}_{32}\text{Ge}$ in the so-called *p*-process:



This process also takes place at the very end of the giant stage of stellar evolution.

The system of nuclear reactions originally proposed by B₂FH (1957) can account for the observed abundances of the chemical elements in the solar system and in nearby stars. Nucleosynthesis is taking place at the present time in the stars of our galaxy and in the stars of other galaxies throughout the universe. We have good evidence in the wavelength spectra of light from distant galaxies that the chemical elements we find on Earth also occur everywhere else in the universe.

However, pulsars and black holes have high internal pressures and temperatures that cause atomic nuclei to disintegrate into more primitive constituents. The relative proportions of the chemical elements in other stars are different because local conditions may affect the yields of the many nuclear reactions that contribute to their synthesis.

2.4 Summary

We live in an expanding universe whose future is uncertain. The universe started with a Big Bang about 15×10^9 years ago and has evolved since then in accordance with the laws of physics.

Stars are the basic units in the hierarchy of heavenly bodies. They form by contraction of clouds of interstellar gas and dust until their core

temperatures are sufficient to cause hydrogen fusion. Stars evolve through predictable stages depending on their masses and initial compositions. They generate energy by nuclear reactions that synthesize other elements from primordial hydrogen and helium. In the end, stars explode, and the remnants become solid objects of great density.

The abundances of the chemical elements in the solar system can be explained by the nuclear reactions that energize the stars. These reactions progress from fusion of hydrogen and helium to neutron capture and to other reactions, most of which occur only for a short time at the end of the active life of a star. The chemical elements we know on Earth occur throughout the universe, but their abundances vary because local conditions affect the yields of the nucleosynthesis processes.

Problems*

1. How has the abundance of hydrogen (H) in the universe changed since the Big Bang?

2. Why are elements with even atomic numbers more abundant than their neighbors with odd atomic numbers?

3. How do we know that the Sun is at least a "second-generation" star?

4. Why do technetium (Tc) and promethium (Pm) lack stable isotopes?

5. What other elements also lack stable isotopes?

6. Why do the elements of Problem 5 exist on the Earth, whereas Tc and Pm do not?

7. Why is lead (Pb) more abundant than we might have expected?

8. Check the abundance of argon (Ar) and determine whether it is greater than expected. If so, suggest an explanation.

9. How did lithium (Li), beryllium (Be), and boron (B) form?

10. Compare the abundances of the "rare earths" (lanthanum to lutetium) to such well-known metals as Ta, W, Pt, Au, Hg, and Pb. Are the rare earths really all that "rare"?

*Not all of these questions have unequivocal answers.

References

- ALPHER, R. A., H. BETHE, and G. GAMOW, 1948. The origin of the chemical elements. *Phys. Rev.*, **73**:803-804.
- ANDERS, E., and M. EBIHARA, 1982. Solar-system abundances of the elements. *Geochim. Cosmochim. Acta*, **46**:2363-2380.

- ATKINSON, R. d'E., and F. G. HOUTERMANS, 1929. Zur Frage der Aufbaumöglichkeit der Elemente in Sternen. *Zeit. Phys.*, **54**:656-665.
- BAADE, W., 1968. *Evolution of Stars and Galaxies*. Harvard University Press, Cambridge, MA.

- BETHE, H. A., 1939. Energy production in stars. *Phys. Rev.*, **55**:434-456.
- BETHE, H. A., 1968. Energy production in stars. *Science*, **161**:541-547.
- BURBRIDGE, E. M., G. R. BURBRIDGE, W. A. FOWLER, and F. HOYLE, 1957. Synthesis of the elements in stars. *Rev. Mod. Phys.*, **29**:547-650.
- FOWLER, W. A., 1967. Nuclear astrophysics. *Amer. Phil. Soc. Mem.* **67**, 109 pp.
- GAMOW, G., 1935. Nuclear transformations and the origin of the chemical elements. *Ohio J. Sci.*, **35**:406-413.
- GAMOW, G., 1952. *The Creation of the Universe*. Viking Press, New York, 144 pp.
- GAMOW, G., 1963. My early memories of Fritz Houtermans. In J. Geiss and E. D. Goldberg (Eds.), *Earth Science and Meteoritics*. North-Holland Publ. Co., Amsterdam, 312 pp.
- GOTT, J. R., III, 1982. Creation of open universes from de Sitter space. *Nature*, **295**:304-307.
- HAINEBACH, K., D. KAZANAS, and D. N. SCHRAMM, 1978. A consistent age for the universe. Short papers of the Fourth International Conference, Geochronology, Cosmochronology and Isotope Geology. *U.S. Geol. Sur. Open-File Rept.*, 78-701, 159-161.
- HEWISH, A., 1975. Pulsars and high density physics. *Science*, **188**:1079-1083.
- HUBBLE, E., 1936. *The Realm of the Nebulae*. Yale University Press, New Haven, CT. Reprinted 1958 by Dover Pub., Inc., New York.
- IBEN, I., Jr., 1967. Stellar evolution: Comparison of theory with observation. *Science*, **155**:785-796.
- IBEN, I., Jr., 1974. Post main sequence evolution of single stars. *Ann. Rev. Astron. and Astrophys.*, **12**:215-256.
- MASON, B., 1962. *Meteorites*. Wiley, New York, 274 pp.
- PENZIAS, A. A., and R. W. WILSON, 1965. A measurement of excess antenna temperature at 4,080 Mc/s. *Astrophys. J.*, **142**:419.
- SCHRAMM, D. N., and W. D. ARNETT, 1973. *Explosive Nucleosynthesis*. University of Texas Press, Austin and London, 301 pp.
- WEINBERG, S., 1977. *The First Three Minutes*. Bantam Books, New York, 177 pp.
- WHEELER, J. C., 1973. After the supernova, what? *Amer. Scientist*, **61**:42-51.

The Solar System

The Sun formed from a cloud of gas and dust particles, as did all other stars in the Milky Way Galaxy and elsewhere in the universe. Sometimes the process leads to the formation of two companion stars. However, in the case of the Sun a small fraction of the original cloud accreted to form a set of nine planets, including the Earth. Compared to stars, these planets are insignificant objects, but to us they are the very basis of existence. The human race appeared on the Earth only two or three million years ago and, after a slow start, learned to fly and to explore the solar system within a span of a mere century.

Geochemistry today not only encompasses the study of the composition and chemical processes occurring on the Earth, but is also concerned with all of the planets and their satellites. Information for geochemical studies of the solar system is derived by analysis of meteorites and rock samples from the Moon and by remote sensing of planetary surfaces. The exploration of the solar system has expanded our horizon and has provided the basis for comparative planetary geochemistry. The satellites of the large gaseous planets are of special interest in this new field of study because some of them are larger than our Moon and have very different chemical compositions and surface features than the Earth.

We therefore need to become acquainted with the new worlds we must explore before we concentrate our attention on the conventional geochemistry of the Earth.

3.1 Origin of the Solar System

The origin of the planets of the solar system is intimately linked to the formation of the Sun. In the beginning there was a diffuse mass of inter-

stellar gas and dust known as the *solar nebula*. It had formed about six billion years ago as a result of the terminal explosions of ancestral stars, which added the elements they had synthesized to the primordial hydrogen and helium that originated from the Big Bang. The chemical composition of the solar nebula was given in Chapter 2 (Table 2.1). The dust cloud was rotating in the same sense of the Milky Way Galaxy and was acted upon by gravitational, magnetic, and electrical forces.

As soon as the main mass of the solar nebula began to contract, order began to be imposed on it by the physical and chemical conditions that existed during this phase of star formation. These included the development of pressure and temperature gradients and an increase in the rate of rotation. Certain kinds of solid particles that had formed in the nebula evaporated as the temperature increased in order to maintain equilibrium between solids and gases. As a result, only the most refractory particles (Fe-Ni alloys, Al_2O_3 , CaO, etc.) survived in the hottest part of the contracting nebula, whereas in the cooler outer regions a larger variety of compounds remained in the solid state. The increase in the rate of rotation caused part of the nebula outside of the protosun to form a central disk. The solid particles congregated in this disk and made it sufficiently opaque to absorb infrared radiation. The temperature in the central disk therefore increased until it ranged from about 2000 K at the center to about 40 K at approximately 7.5×10^9 km from the protosun. The pressure ranged from less than 0.1 atm to about 10^{-7} atm near the edge of the disk (Cameron, 1978; Cameron and Pine, 1973).

The development of pressure and temperature gradients within the disk caused the first

major chemical differentiation of the solar nebula. Compounds with low vapor pressures persisted throughout the nebula and formed “dust” particles, whereas compounds with high vapor pressures could exist only in the cooler outer regions. The condensation temperatures of various compounds that existed in the solar nebula are listed in Table 3.1. The condensates accreted to form larger bodies as a result of selective adhesion caused by electrostatic and magnetic forces. The resulting solid bodies, called *planetesimals*, had diameters ranging from about 10 m to more than 1000 km, and their chemical compositions varied with distance from the center of the planetary disk. The planetesimals close to the protosun were composed of refractory compounds dominated by oxides and metallic iron and nickel; farther out were Mg and Fe silicates and farthest out, ices composed of water, ammonia, methane, and other volatiles.

The initial rate of evolution of the solar system was remarkably fast. The time required for the Sun to reach the ignition temperature for

hydrogen fusion was less than 100,000 years. The Sun’s initial luminosity was two to three times greater than is consistent with the main sequence because the Sun contained excess thermal energy generated during the initial contraction. This “superluminous” phase of the Sun lasted about 10 million years and resulted in the expulsion of about 25% of its original mass in the form of “solar wind” composed of a proton/electron plasma. This is called the “T-Tauri stage” of stellar evolution after the star that is the prototype for this process. All gaseous matter in the vicinity of the Sun was blown away during this period, and only the solid planetesimals having diameters larger than about 10 m remained.

The planetesimals in the inner region of the planetary disk subsequently accreted to form the so-called earthlike planets—Mercury, Venus, Earth, and Mars—and the parent bodies of the meteorites now represented by asteroids. Instabilities in the outer part of the disk resulted in the formation of the gaseous outer planets: Jupiter, Saturn, Uranus, Neptune, and Pluto.

Table 3.1 Condensates from the Solar Nebula at Different Temperatures

Temperature, °C	Condensates
1325	refractory oxides: CaO, Al ₂ O ₃ , TiO ₂ , REE oxides
1025	metallic Fe and Ni
925	enstatite (MgSiO ₃)
925–220	Fe forms FeO, which reacts with enstatite to form olivine [(Fe,Mg) ₂ SiO ₄]
725	Na reacts with Al ₂ O ₃ and silicates to form feldspar and related minerals. Condensation of K and other alkali metals
400	H ₂ S reacts with metallic Fe to form troilite (FeS)
280	H ₂ O vapor reacts with Ca-bearing minerals to make tremolite
150	H ₂ O vapor reacts with olivine to form serpentine
–100	H ₂ O vapor condenses to form ice
–125	NH ₃ gas reacts with water ice to form solid NH ₃ · H ₂ O
–150	CH ₄ gas reacts with water ice to form solid CH ₄ · 7H ₂ O
–210 ^a	Ar and excess CH ₄ condense to form Ar and CH ₄
–250 ^a	Ne, H, and He condense

^aThese reactions probably did not occur because the temperature in the planetary disk did not decrease to such low values.

SOURCE: Glass (1982), based on Lewis (1974).

The origin and chemical composition of Pluto are still not well known because this planet is difficult to observe from Earth. Pluto also does not conform to the so-called *Titius-Bode law*, which appears to govern the distances of the planets from the Sun when these are expressed in *astronomical units* (A. U.), defined as the average distance between the Earth and Sun. The Titius-Bode law was published in 1772 by J. E. Bode, director of the Astronomical Observatory in Berlin, and is based on a series of numbers discovered by J. D. Titius of Wittenberg in 1766. The series is composed of the numbers 0.4, 0.7, 1.0, 1.6, 2.8, . . . , which are obtained by writing 0, 3, 6, 12, 24, . . . , adding 4 to each number, and dividing by 10. The resulting numbers match the distances of the planets from the Sun remarkably well up to and including Uranus (Mehlin, 1968). However, the radius of the orbit of Neptune is only 30.1 A.U., whereas the Titius-Bode value is 38.8 and the discrepancy in the case of Pluto is even greater (Table 3.2). The Titius-Bode law predicts a value of 77.2, but the actual orbital radius of Pluto is only 39.4 A.U. The discrepancy may suggest that Pluto did not form in the orbit it now occupies.

The descriptive physical properties of the solar system listed in Table 3.2 indicate that 99.87% of the total mass of the solar system (2.052×10^{33} g) is concentrated in the Sun. The remaining 0.13% is distributed among the nine major planets, among which Jupiter is by far the largest with about 71% of the planetary masses. The densities and sizes of the planets, shown in Figure 3.1, vary widely and imply the existence of large differences in their chemical compositions. The inner planets (Mercury, Venus, Earth, and Mars), as well as the Moon and the asteroids, are solid objects composed primarily of elements and compounds having low vapor pressures. The outer planets (Jupiter, Saturn, Uranus, and Neptune) have low densities and are essentially gaseous, although all of them probably have condensed cores. The inner planets resemble the Earth in chemical composition and are therefore referred to as the *terrestrial* or *earthlike* planets. The outer planets consist primarily of hydrogen and helium with small amounts of the other elements and resemble the Sun in chemical composition.

The earthlike planets (plus the Moon and asteroids), taken together, make up only 0.0006% of the total mass of the solar system and only

Table 3.2 Properties of the Sun and Her Planets

Object	Mean solar distance		Equatorial diameter, km	Mass, g	Density g/cm ³	Number of satellites
	10 ⁶ km	A. U.				
Sun	—	—	1,391,400	1.987×10^{33}	1.4	—
Mercury	57.9	0.387	4,878	3.30×10^{26}	5.44	0
Venus	108.2	0.723	12,100	4.87×10^{27}	5.25	0
Earth	149.6	1.00	12,756	5.98×10^{27}	5.52	1
Moon	—	—	3,476	7.35×10^{25}	3.34	—
Mars	227.9	1.52	6,786	6.44×10^{26}	3.94	2
Ceres (asteroid)	414.0	2.77	1,020	1.17×10^{24}	2.2	—
Jupiter	778.3	5.20	142,984	1.90×10^{30}	1.33	16
Saturn	1,427.0	9.54	120,536	5.69×10^{29}	0.70	21
Uranus	2,869.6	19.2	51,118	8.66×10^{28}	1.30	15
Neptune	4,504	30.1	49,562	1.0123×10^{29}	1.76	8
Pluto	5,900	39.4	3,000	1.5×10^{25}	1.1	1

SOURCE: Carr et al. (1984), Glass (1982), and fact sheet, Jet Propulsion Laboratory.

0.44% of the planetary masses. All of these objects are so close to the Sun that the orbital radius of the outermost asteroid is only about 7% of the total radius of the solar system. Evidently, the terrestrial planets are not typical of the solar system and owe their existence to the special conditions in the planetary disk close to the Sun. Earth is the largest of the inner planets with about 50.3% of the mass, followed by Venus (40.9%), Mars (5.4%), and Mercury (2.8%).

The earthlike planets, viewed in Figure 3.1 in the perspective of the entire solar system, are a physical and chemical anomaly. The Earth is unique among its earthlike neighbors in having about 71% of its surface covered by liquid water within which life developed early in its history and evolved into the multitude of species of the plant and animal kingdoms. Insofar as we know, life forms do not exist at the present time anywhere else in the solar system.

3.2 Origin of the Earthlike Planets

Our current understanding of the origin of the solar system indicates that the earthlike planets were hot when they formed and that their internal geochemical differentiation may have begun with the *sequential accretion* of planetesimals of differing compositions (Murray et. al., 1981). Planetesimals composed of metallic iron and oxides accreted first to form a core that was subsequently buried by the planetesimals composed of silicates. The earthlike planets were initially molten because of the heat generated by the rapid capture of the planetesimals and because of radioactive heating.

The last phase of formation of Earth, Venus, and Mars involved the capture of planetesimals composed of volatile compounds that had formed in the outer reaches of the planetary disk, perhaps

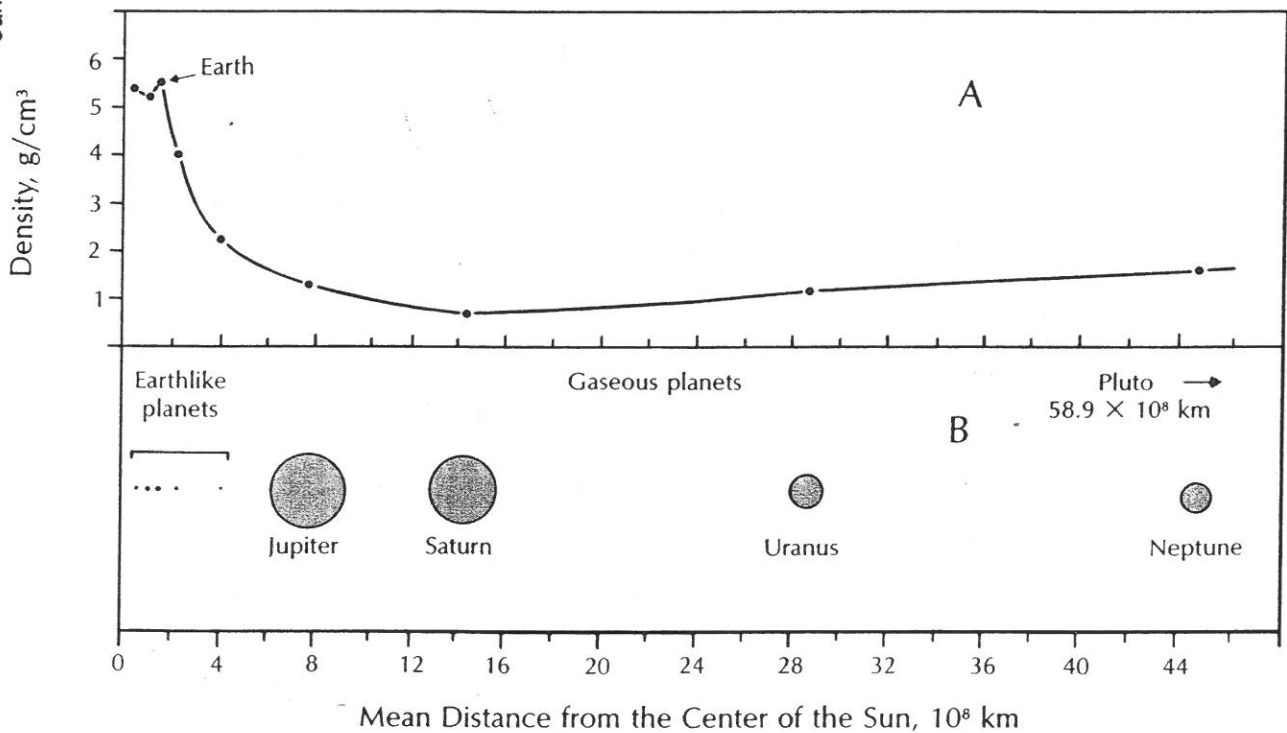


Figure 3.1 A: Variation of density of the planets with mean distance from the Sun. Note that the Earth has the highest density among the earthlike planets, which, as a group, are more dense than the outer gaseous planets. **B:** The planets of the solar system magnified 2000 times relative to the distance scale. The earthlike planets are very small in relation to the Sun and the gaseous planets of the solar system.

beyond the orbit of Jupiter. These volatile-rich planetesimals, also known as *cometesimals*, deposited solids composed of water, ammonia, methane, and other volatiles on the surfaces of the planets. The water and other volatiles deposited on the Earth promptly evaporated to form a dense atmosphere from which water ultimately condensed as the surface of the Earth cooled. Mercury and the Moon do not have atmospheres partly because they are too small to retain gaseous elements of low atomic number and their compounds.

According to this scenario, the earthlike planets have been cooling since the time of their formation. Mercury and the Moon have cooled sufficiently to become geologically "inactive" in the sense that their interiors no longer interact with their surfaces. Venus and Earth, being the largest of the earthlike planets, have retained more of the initial heat than their neighbors in the solar system and are still active. Mars is intermediate in size and has had volcanic eruptions in the not-too-distance geologic past. However, the age of the last martian volcanism is not known.

In spite of the similarity in size and overall composition of Venus and Earth, their surfaces have evolved very differently. Venus has a dense atmosphere composed of CO_2 that has caused its surface to become extremely hot and dry. The surface of Earth cooled rapidly, allowing oceans

to form more than 4×10^9 years ago by condensation of water vapor in the atmosphere. The presence of a large volume of water on the surface of Earth permitted geological processes to operate and created conditions conducive to the development and evolution of life. Neither the Earth nor any of the earthlike planets ever had atmospheres composed of the hydrogen and helium of the solar nebula because these gases were expelled from the inner region of the solar system during the T-Tauri stage of the Sun.

3.3 Satellites of the Outer Planets

All of the outer planets have satellites, some of which are larger than the Moon and the planet Mercury. In addition, these satellites have a wide range of chemical compositions and have responded in very different ways to the forces acting on them. The large satellites of Jupiter were seen by Galileo Galilei on January 7, 1610, with his newly built telescope. Actually, they may have been observed even earlier by Simon Marius. However, detailed images of their surfaces were obtained only recently during "flybys" of the American Pioneer and Voyager space probes. A chronology of these events in Table 3.3 reveals the sudden burst of activity in the exploration of the solar system between 1973 and 1989.

Table 3.3 Chronology of Exploration of the Satellites of Jupiter and Saturn

<i>Planet</i>	<i>Encounter date</i>	<i>Spacecraft</i>	<i>Comments</i>
Jupiter	Dec. 3, 1973	Pioneer 10	left solar system on June 14, 1983
Jupiter	Dec. 2, 1974	Pioneer 11	continued to Saturn
Jupiter	March 5, 1979	Voyager 1	1408 images of jovian satellites
Jupiter	July 9, 1979	Voyager 2	1364 images of jovian satellites
Jupiter	Dec. 7, 1995	Galileo	mission in progress in 1997
Saturn	Sept. 1, 1979	Pioneer 11	low-resolution images
Saturn	Nov. 13, 1980	Voyager 1	900 images of saturnian satellites
Saturn	Aug. 26, 1981	Voyager 2	1150 images of saturnian satellites
Uranus	Jan. 25, 1986	Voyager 2	images of all satellites as well as the rings
Neptune	Aug. 25, 1989	Voyager 2	images of the planet and its satellite Triton

After Greeley (1985).

The planet Jupiter has 16 satellites and a ring guarded by two small satellites. The so-called Galilean satellites Io, Europa, Ganymede, and Callisto were actually named by Marius after mythological lovers of the Greek god Zeus whose Latin name was Jupiter. A fifth satellite was discovered 282 years later by Barnard who named it Amalthea after a nymph who once nursed Jupiter. These satellites, together with three small ones found in 1979, move in nearly circular orbits close to the equatorial plane of Jupiter. Four small satellites (Leda, Himalia, Lysithea, and Elara) are located about 11 million km from Jupiter and have eccentric orbits that are inclined nearly 30° to its equatorial plane. A third group (Ananke, Carme, Pasiphaë, and Sinope) at a distance of about 22 million km from Jupiter have retrograde orbits whose inclination is between 150° and 160° . The Galilean satellites form in effect a small-scale planetary system of their own with Jupiter as their central "star." Their densities, listed in Table 3.4 and displayed in Figure 3.2, decrease with increasing orbital radius from 3.53 (Io) to 1.79 (Callisto) g/cm^3 ; therefore they are believed to have significantly different chemical compositions.

Io is composed primarily of silicate material and may have an iron sulfide core. Before the encounters with the Voyager spacecraft, Peale et al. (1979) calculated the amount of heat generated within Io by tidal friction caused by the gravitational pull of Jupiter and Europa and predicted that active volcanoes may be present. This prediction was supported by images sent back by Voyager 1 on March 9, 1979, which indicated that the surface of this planet was *not* cratered as had been expected. Subsequently, Morabito et. al. (1979) discovered a huge volcanic eruption on Io that was obliterating impact craters and all other topographic features in a large area surrounding the volcano. Eventually, nine active volcanoes were identified and named after mythological deities associated with fire (Amirani, Loki, Marduk, Masubi, Maui, Pele, Prometheus, Surt, and Volland). The volcanic plumes contain sulfur dioxide and the lava flows may be composed of liquid sulfur, consistent with the fact that the sur-

face of Io is yellow to red in color. The surface heat flow of Io is about 48 microcalories/ cm^2/sec and is therefore about 30 times greater than that of the Earth. Io is clearly the most volcanically active object in the solar system.

The other Galilean satellites of Jupiter (Europa, Ganymede, and Callisto) have lower densities than Io and are composed of silicate material with crusts of water ice and mantles of liquid water. They are not volcanically active at the present time, and their surfaces are cratered. Europa appears to be completely covered by a frozen ocean 75–100 km deep. The icy crust may be underlain by liquid water that does not freeze because of heat generated by tidal friction. The surface of Europa is crisscrossed by a multitude of curving bands, some of which have been traced for more than 1000 km. The bands appear to be fractures in the crust caused by internal tectonic activity and by meteorite impacts. The fractures were subsequently filled with sub-crustal water that froze to form ice dikes.

Ganymede is larger than the planet Mercury and appears to be composed of water and silicate material in about equal proportions. Its surface is composed of water ice mixed with impurities that cause it to darken in color. The dark terrains are fragmented and more heavily cratered than the light-colored terrain in which they are embedded. The ice crust is about 100 km thick and is underlain by a mantle of liquid water between 400 and 800 km deep. The water may have intruded the crust locally in the form of ice slush to produce intrusive bodies of water ice.

Callisto is the outermost of the Galilean satellites. It is darker in color than the others and has a heavily cratered icy crust about 200 km thick. A prominent feature on its surface is a very large multiringed basin called *Valhalla* whose diameter is nearly 2000 km. A second ringed basin near the north pole is called *Asgard*. The icy crust may be underlain by a liquid mantle about 1000 km thick composed of water. Callisto apparently became inactive very early in its history partly because the amount of heat generated by tidal friction is less than that of the other Galilean satellites. In

Table 3.4 Physical Properties of the Major Satellites of Jupiter, Saturn, Uranus, and Neptune

<i>Name</i>	<i>Mean distance from planet, km</i>	<i>Diameter, km</i>	<i>Mass, g</i>	<i>Density, g/cm³</i>
Jupiter				
Io	421,600	3,640	8.91×10^{25}	3.53
Europa	670,900	3,130	4.87×10^{25}	3.03
Ganymede	1,070,000	5,280	1.49×10^{26}	1.93
Callisto	1,883,000	4,840	1.06×10^{26}	1.79
Saturn				
Mimas	188,000	390	$(3.7 \pm 0.1) \times 10^{22}$	1.2
Enceladus	240,000	500	$(7.4 \pm 3.4) \times 10^{22}$	1.1
Tethys	297,000	1,050	$(6.26 \pm 0.17) \times 10^{23}$	1.0
Dione	379,000	1,120	$(1.05 \pm 0.03) \times 10^{24}$	1.42
Rhea	528,000	1,530	$(2.16 \pm 0.7) \times 10^{24}$	1.3
Titan	1,221,000	5,140	$(1.348 \pm 0.017) \times 10^{26}$	1.9(+)
Hyperion	1,502,000	~ 290		
Iapetus	3,559,000	1,440	$(2.8 \pm 0.7) \times 10^{24}$	1.2
Phoebe	10,583,000	160		
Uranus				
Miranda	130,000	470	7.34×10^{22}	1.35
Ariel	192,000	1,150	1.32×10^{24}	1.66
Umbriel	267,000	1,170	1.26×10^{24}	1.51
Titania	438,000	1,580	3.47×10^{24}	1.68
Oberon	586,000	1,520	2.90×10^{24}	1.58
Neptune				
Triton	354,000	3,000	9.273×10^{25}	
Nereid	5,510,000	~940	1.3×10^{18}	

Data from Glass (1982), Greeley (1985), Hunt and Moore (1981), Hamblin and Christiansen (1990), and fact sheet, Jet Propulsion Laboratory.

addition, less heat is generated by radioactivity because its rocky core is relatively small.

The satellites of Saturn, Uranus, and Neptune are identified in Table 3.4. All of them were "seen" during flybys of Voyager 2. We will mention only Titan, the largest of the satellites of Saturn. It has a dense atmosphere composed principally of methane, nitrogen, and smaller amounts

of other gases including ethane, acetylene, ethylene, and hydrogen cyanide. Like the Gallilean satellites of Jupiter, each of the satellites of Saturn, Uranus, and Neptune is a unique body in the solar system that has recorded on its surface a history of events caused by internal and external processes. Images and remote-sensing data of these satellites were received only recently during

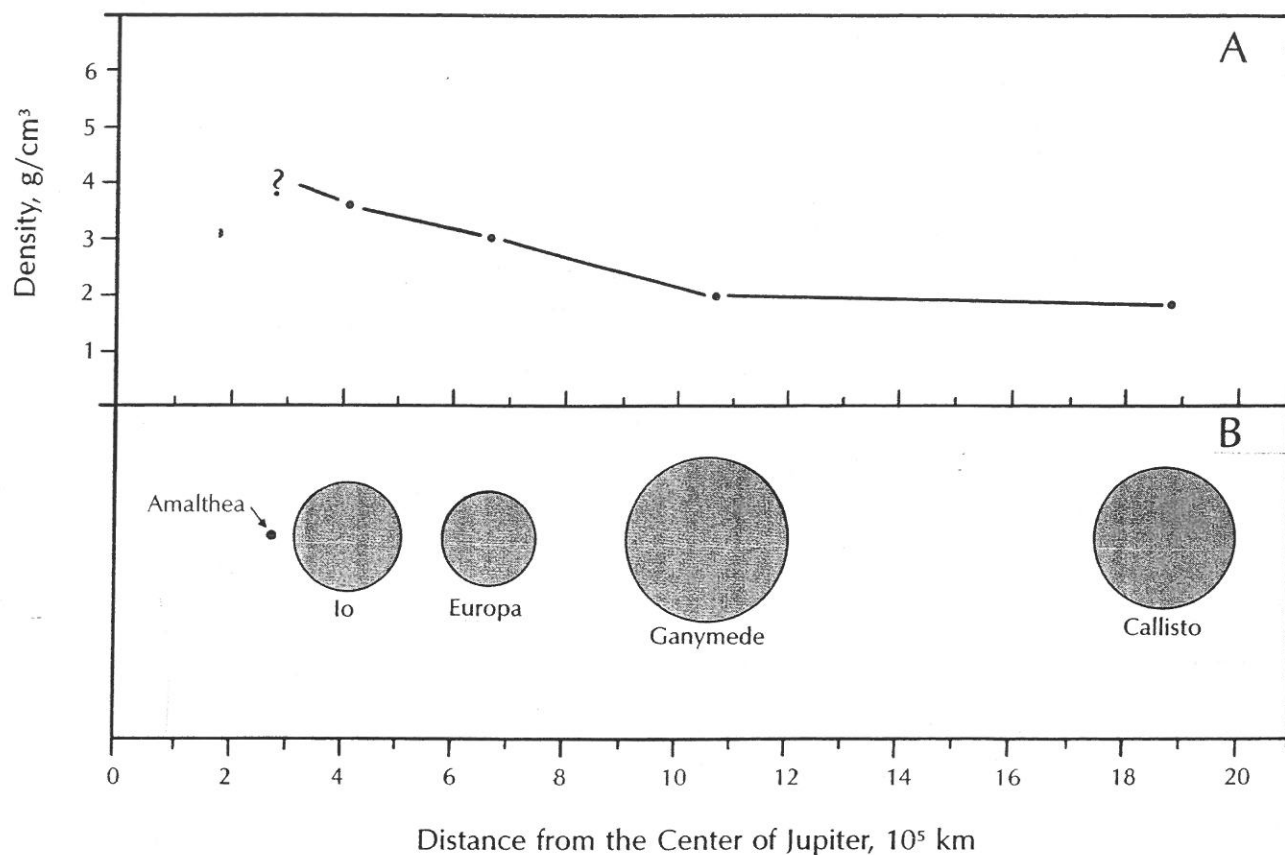


Figure 3.2 A: Variation of the density of the Galilean satellites of Jupiter with increasing distance from the planet. The decrease in density is caused by increases in the proportion of water relative to silicate material. **B:** The Galilean satellites magnified 50 times relative to the distance scale. Amalthea is much smaller than Io but appears to be a silicate object.

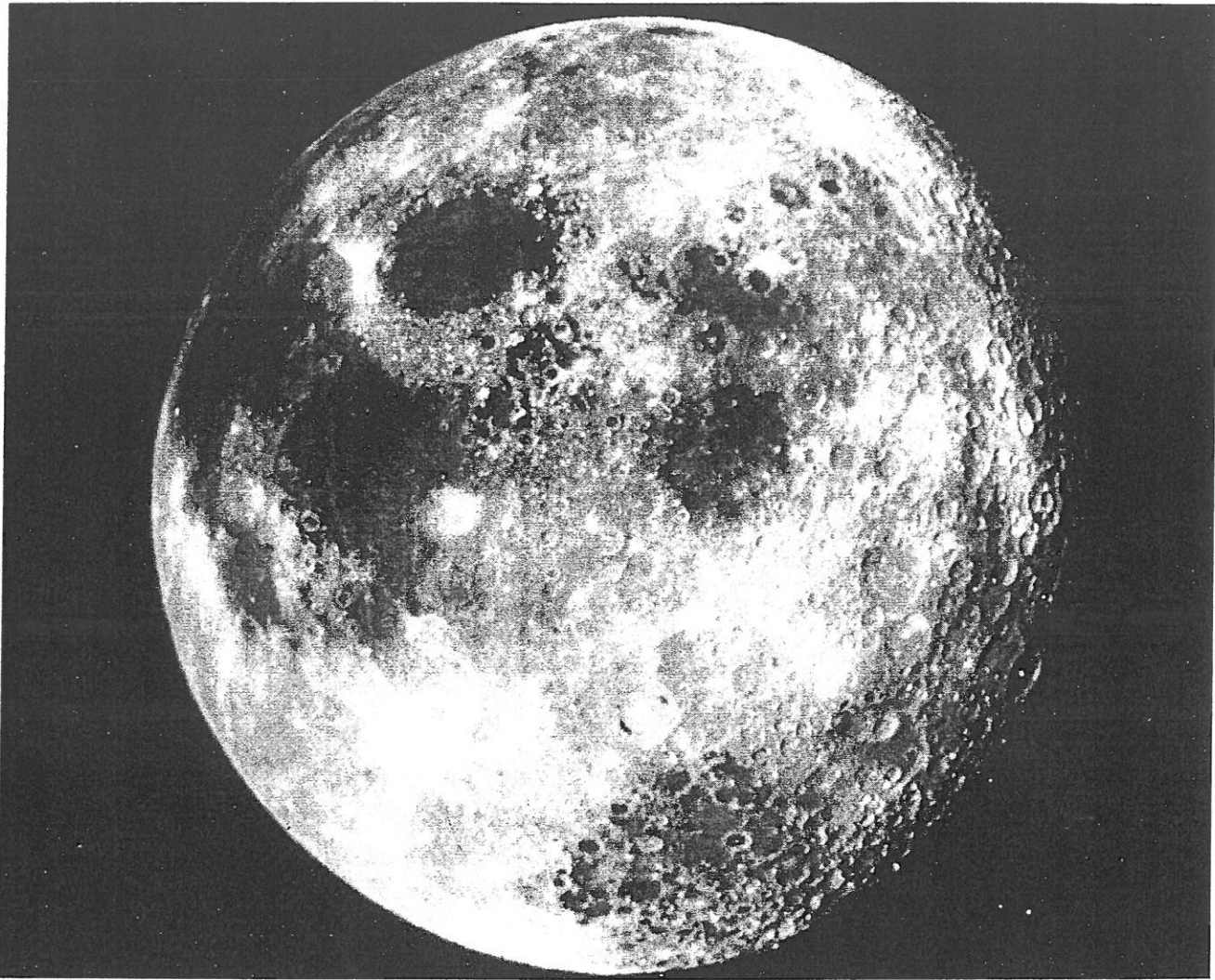
the flyby of the Voyager space probes in 1981 (Saturn), 1986 (Uranus), and 1989 (Neptune).

3.4 Pictures of Our Solar System

The exploration of the solar system relies primarily on unmanned space probes that have the capability of taking pictures of planetary surfaces and of returning the images to Earth. The two Viking landers and the Pathfinder mission on Mars, as well as the two Voyager spacecraft and the spacecraft Galileo in the Jupiter system are spectacular examples of this technique, whereas the Moon has been explored primarily by American astronauts who actually walked on its surface.

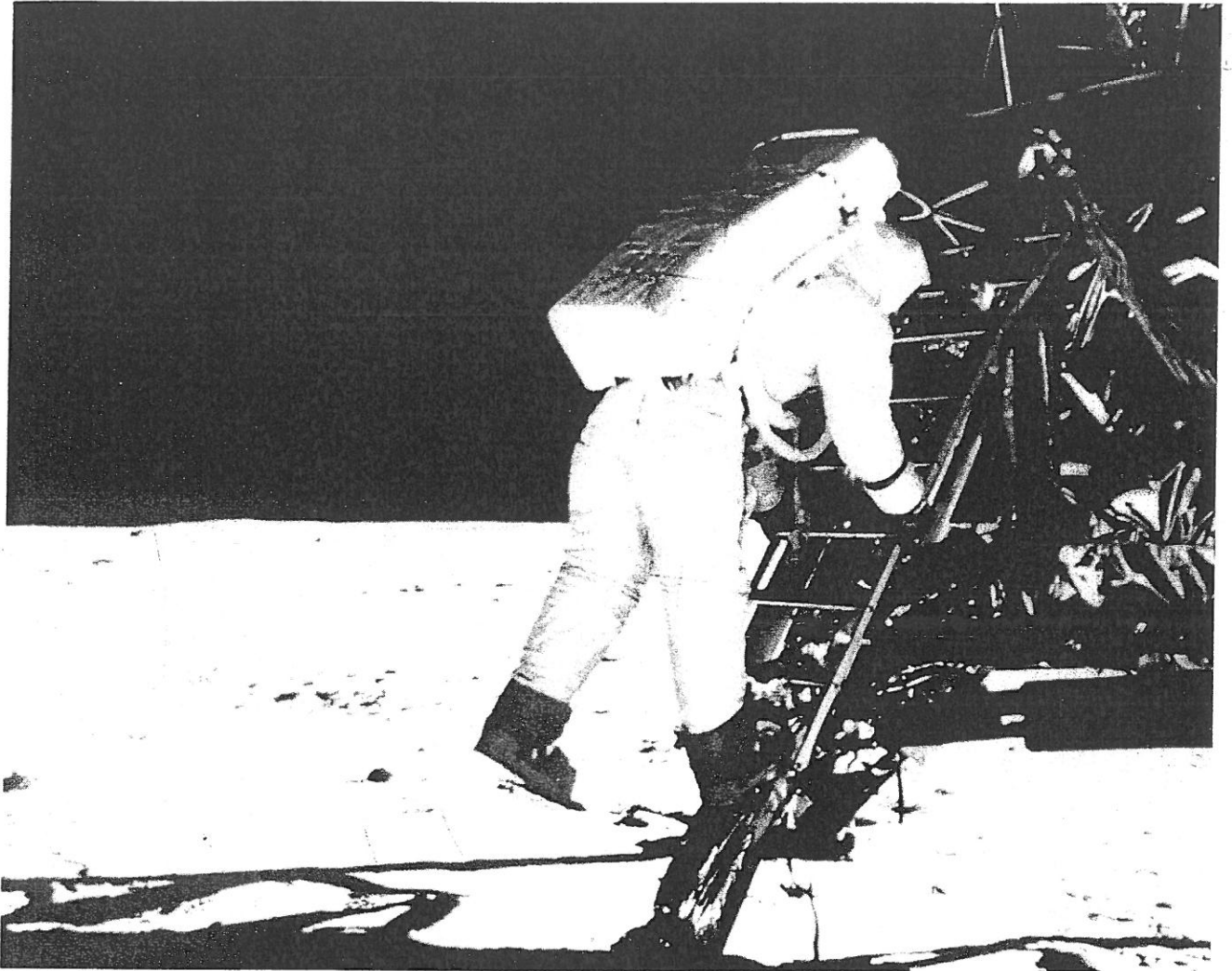
The exploration of the new worlds, which are suddenly within our reach, will become an important task of the community of Earth Scientists. Although an understanding of these new worlds must ultimately be based on studies of the chemical compositions of matter and of reactions and processes that take place on them, images of the surfaces of planets help to identify the problems that need to be solved.

For this reason, we now examine some of the images of our solar system to confront the challenge that lies ahead. Excellent photographs of landforms on planetary surfaces appear in textbooks by Hamblin and Christiansen (1990) and by Greeley (1985).

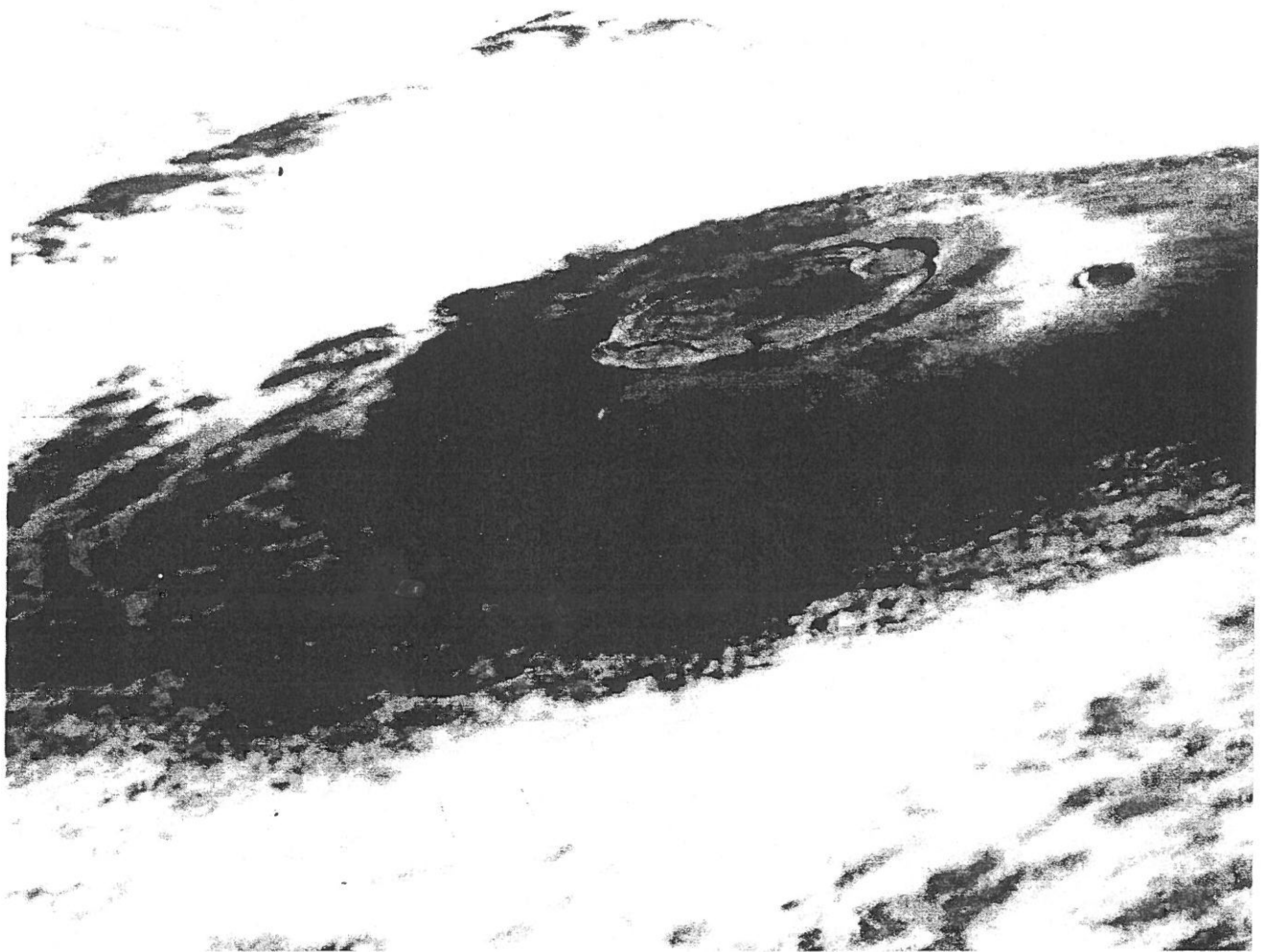


The Moon is a familiar image in the sky. Its surface is pockmarked with craters formed by impacts of meteoroids, which continue to fall, though at a greatly reduced rate. The lunar landscape consists of dark plains, called mare (singular) and maria or mares (plural), and bright mountainous highlands. The mare basins, formed by impacts of large objects during the early history of the Moon, are filled with sheetlike basalt flows. The highlands are older than the mare basins and are composed of anorthositic gabbro. The surface of the Moon is covered by a layer of regolith (colloquially called "soil") that consists of rock and mineral particles, beads of impact glass, and chunks of regolith breccia.

This view of the Moon was taken from space by the astronauts of Apollo 17 in December 1972. It shows the roughly circular, black Mare Crisium in the left upper quadrant. Southwest of Mare Crisium is the Mare Fecunditatis, and directly west of Crisium is the Mare Tranquilitatis. The Mare Serenitatis is located northwest of Tranquilitatis and extends northwesterly beyond the horizon. (Photo by NASA.)



In the late evening of July 20, 1969 (EDT on Earth), Neil A. Armstrong and Edwin E. Aldrin descended from their spacecraft and set foot on the surface of the Moon. They had landed near the southwest margin of the Sea of Tranquility (Mare Tranquilitatis). The picture shows Edwin Aldrin on his way down just before he stepped onto the lunar surface. The dusty plain in the background contains scattered boulders ejected from craters excavated by impact of meteoroids. (Photo by NASA.)



The surface of the planet Mars comes closest among all the planets in the solar system to the landscapes of Earth. Mars has an atmosphere composed of N_2 and CO_2 with a small amount of water. It also has roughly circular plains called planitia and highly cratered highlands resembling those of the Moon. Mars has been an active planet, as indicated by large shield volcanoes and rift valleys. In some places on Mars the surface is dissected by valleys in dendritic patterns similar to stream valleys on Earth. Therefore, there is reason to believe that liquid water has existed on the surface of Mars and that ice, in the form of permafrost, may still occur on Mars at the present time.

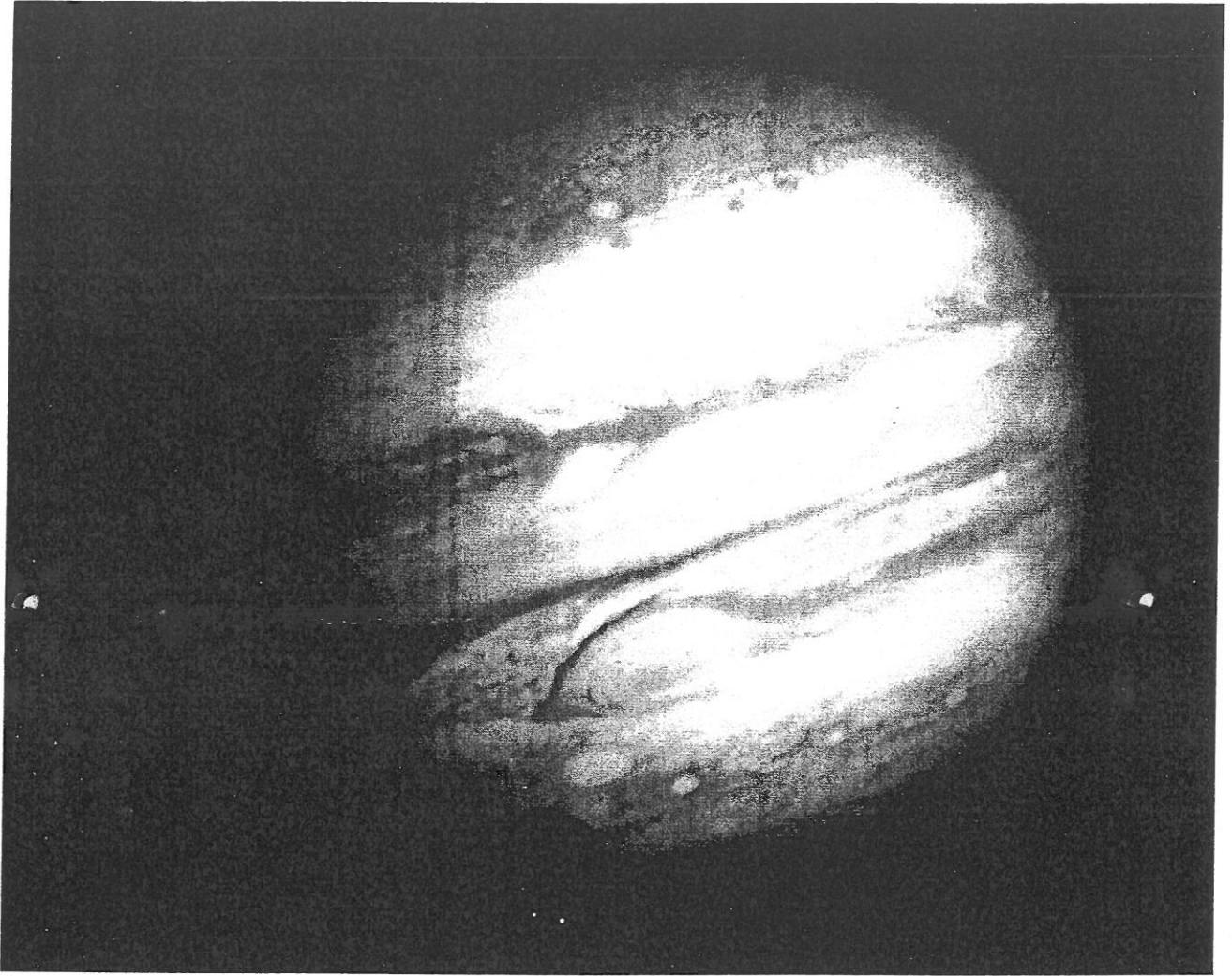
The picture shows the summit of the volcano Olympus Mons protruding through clouds on a frosty morning on Mars much like Mauna Loa on the island of Hawaii. The summit contains several overlapping calderas whose presence suggests a long history of volcanic activity. The volcano is 550 km in diameter at its base, and it rises 25 km above the surrounding plain—far higher than any mountain on Earth. (Photo by NASA.)



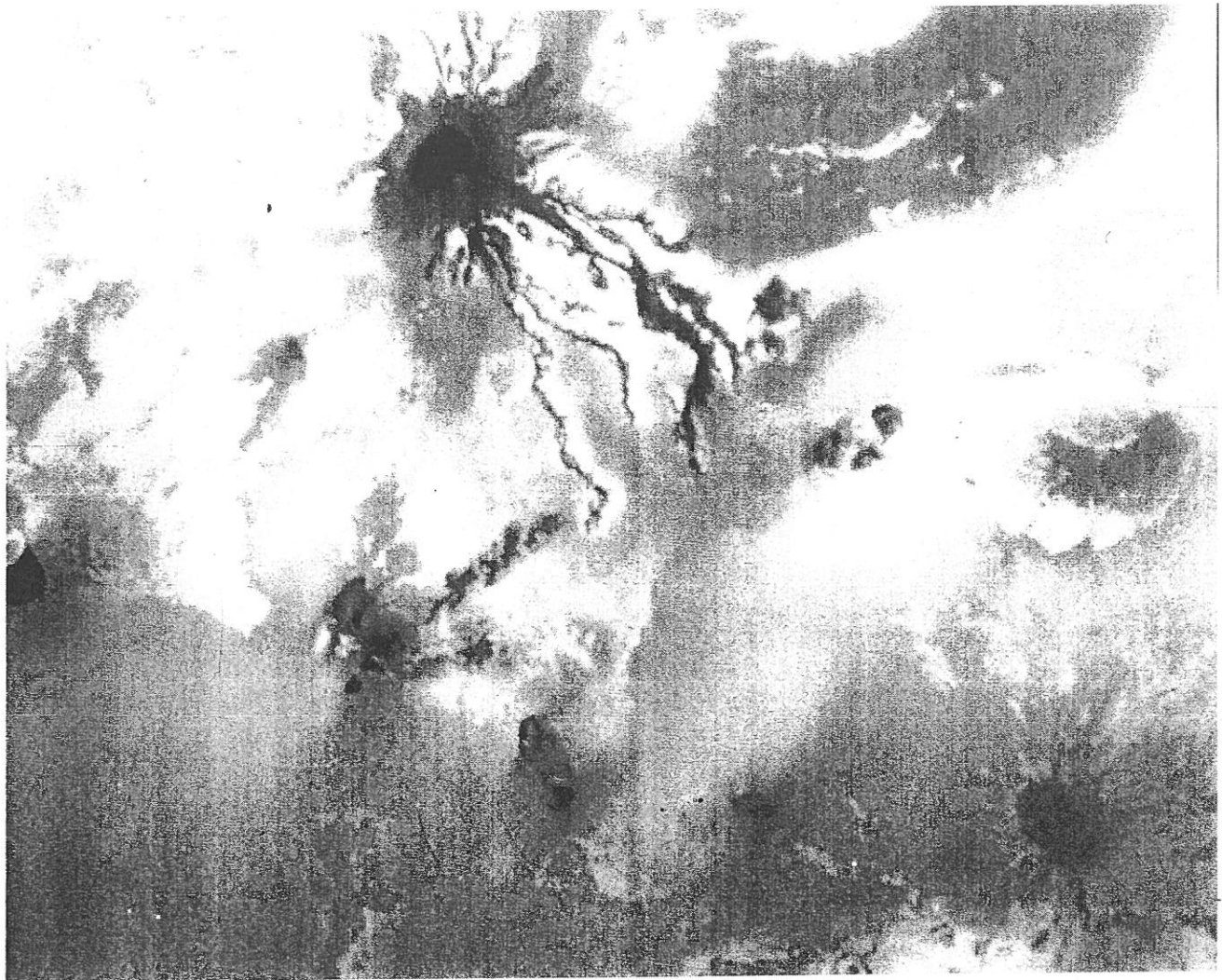
The Valles Marineris on Mars, which are probably rift valleys, extend more than 2400 km in an east-west direction near the martian equator. Some of the valleys are up to 200 km wide and 7 km deep. The walls of the valleys have been extensively modified by slides and by erosional channels. The rocks into which the valleys are cut are layered and may be sheetlike flows of basalt. (Photo by NASA.)



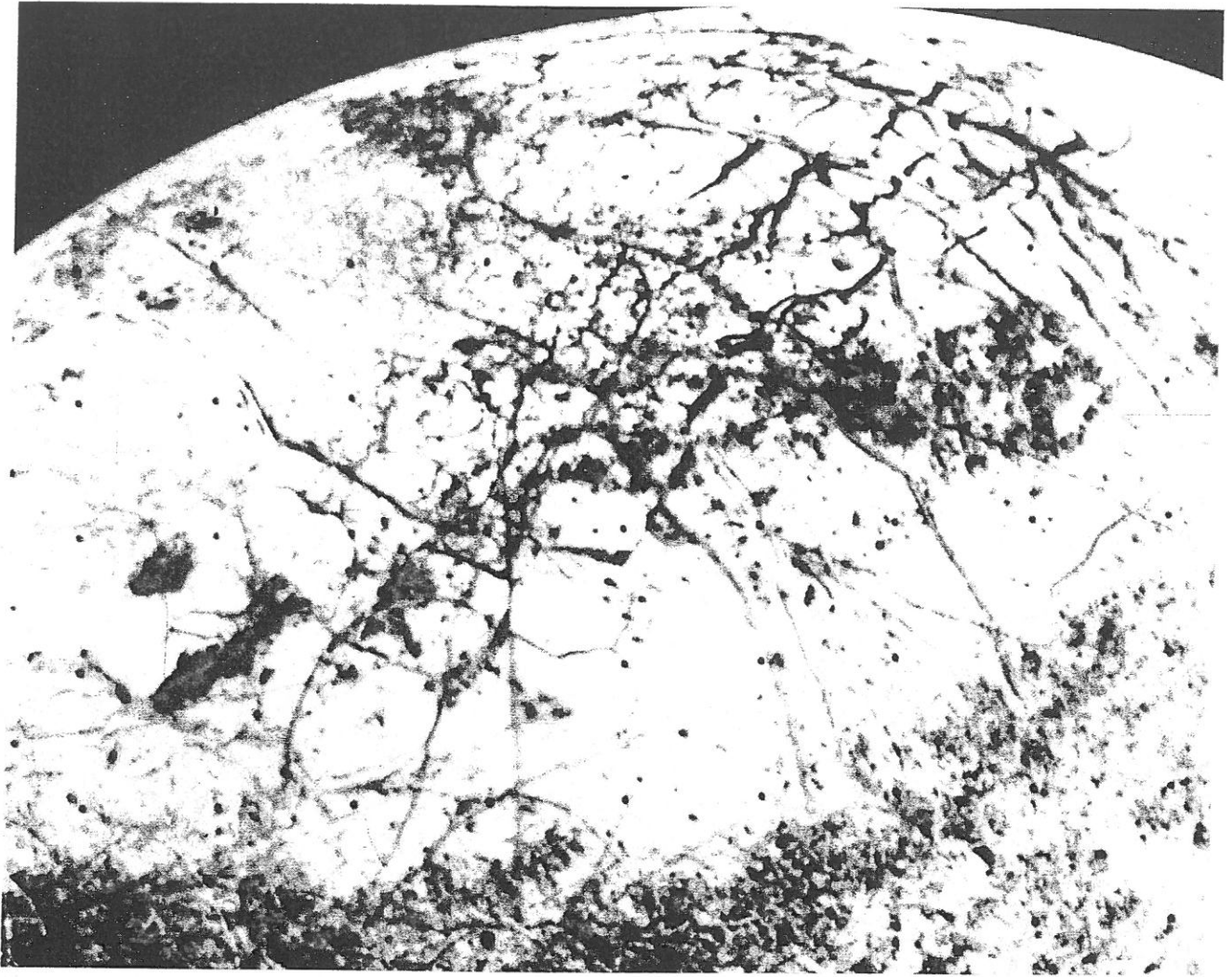
The first Viking lander touched down on Mars in Chryse Planitia on July 20, 1976. As shown, this area is a stony desert containing small sand dunes and angular boulders. The view at the landing site of Viking 2 in the Utopia Planitia is quite similar, indicating the importance of wind in shaping the surface of Mars. Some of the boulders are pitted or vesicular, perhaps because they originated from underlying lava flows. (Photo by NASA.)



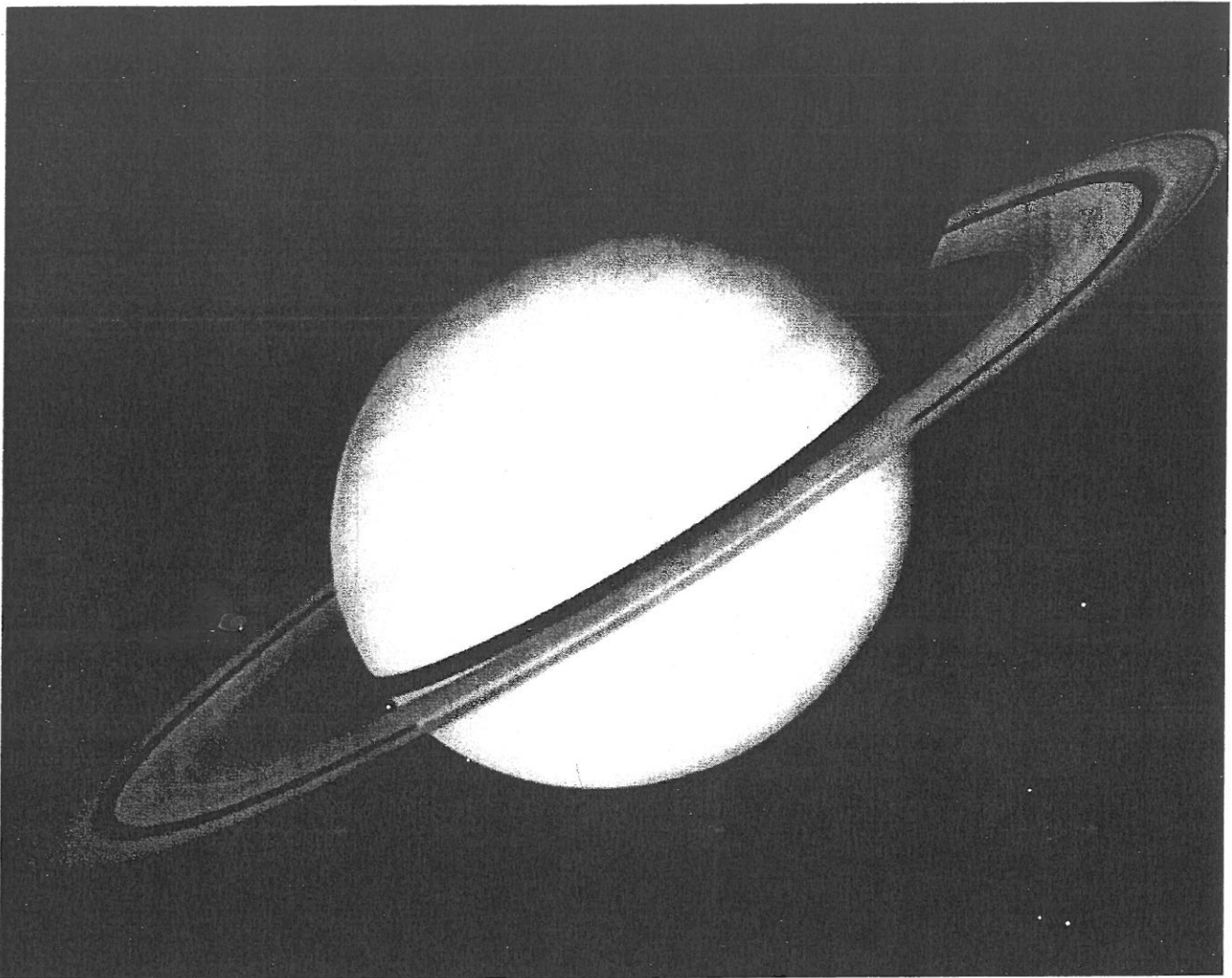
Jupiter is by far the largest and most massive of the planets in the solar system. It has a turbulent atmosphere that contains several cyclonic storm centers, including the "Great Red Spot." The atmosphere is composed primarily of hydrogen and helium with small amounts of other elements of higher atomic number. Jupiter is not massive enough to initiate hydrogen fusion in its core. Nevertheless, it has several sets of satellites, and some of the satellites are comparable in size to the Moon of the Earth. (Photo by NASA.)



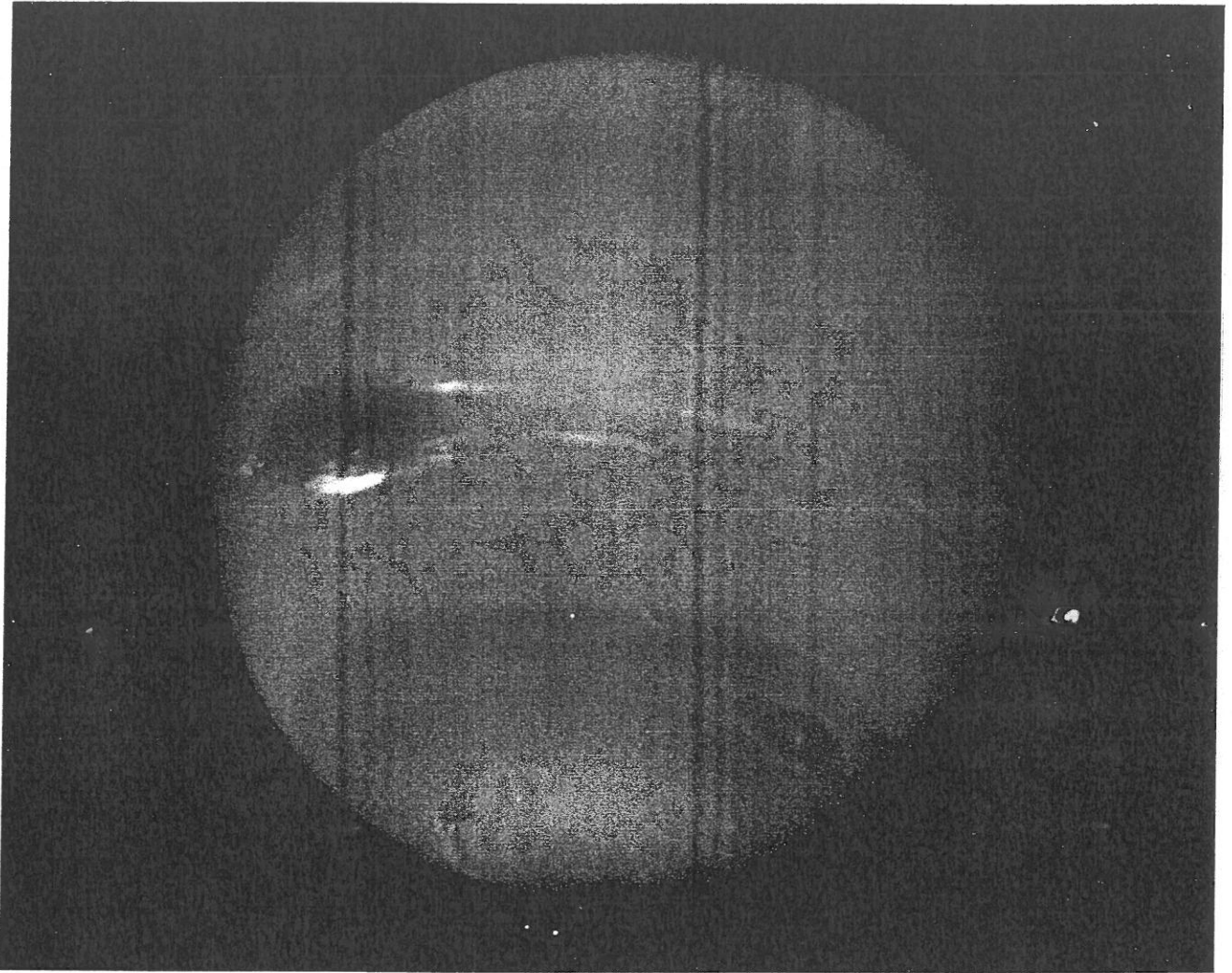
Io is the innermost of the so-called Galilean satellites of Jupiter. It is probably composed of silicate rocks like the Moon and Mars, but its many active volcanoes emit sulfur-rich lavas and gases. The surface of Io is not cratered because impact craters are quickly buried by lava flows and volcanic ash. The heat that causes the volcanic activity is generated by tidal forces caused by the gravitational fields of Jupiter and Europa, the neighbor of Io. (Photo by NASA.)



Europa is the second of the Galilean satellites of Jupiter. Unlike Io, Europa is encased in a layer of water ice beneath which liquid water may be present. The icy surface is cut by sets of lines that may be fractures filled with "ice-dikes" from below. Impact craters are present but are not common, presumably because of periodic renewal of the surface of extrusion of water through the system of fractures. The interior of Europa consists of silicate rocks and a small dense core. Ganymede and Callisto, the other two Galilean satellites, are also ice-covered, but each is distinctly different from its neighbors. (Photo by NASA.)



Saturn is justly famous for its intricate rings, although all of the gaseous planets are now known to have rings. Saturn, like Jupiter, has a retinue of satellites, the largest of which is Titan. This satellite is only slightly smaller than Ganymede and has an atmosphere composed mainly of nitrogen with some methane and other hydrocarbon gases. Because of the low surface temperature on Titan, most of the methane (or ethane, C_2H_6) may form oceans of liquid hydrocarbons. (Photo by NASA.)



Neptune, the last of the great gaseous planets, was photographed in August 1989 by Voyager 2. It is blue in color and has a turbulent atmosphere like that of Jupiter in spite of its great distance from the Sun (more than 4×10^9 km) and its much smaller size compared to Jupiter (about 6%). Neptune has at least eight satellites, Triton being the most massive. The surface temperature of Triton is only 37 K or -236°C . Nevertheless, cryovolcanic activity is occurring on Triton involving the eruption of liquid N_2 and perhaps methane. Consequently, the surface of Triton contains few impact craters and is composed of landforms never seen before on any satellite. (Photo by NASA.)



Planet Earth is our home in the solar system. It is the only planet or satellite with liquid water on its surface and with an atmosphere containing molecular oxygen. Earth is also the only place in the solar system that can sustain life as we know it.

This view of the southern hemisphere showing Africa, the Indian Ocean with Madagascar, and the Atlantic Ocean was taken from space by the astronauts of Apollo 17, December 1972. (Photo by NASA:)

3.5 Summary

The sequence of events leading to the formation of the solar system can be reconstructed as a direct extension of stellar evolution by applying the laws of physics and chemistry to a diffuse cloud of gas and dust particles in interstellar space.

The earthlike planets constitute a very small fraction of the total mass of the solar system and are dwarfed even by the outer gaseous planets. Nevertheless, Earth is the only planet in the entire solar system on which the surface environ-

ment is conducive to the development and evolution of life forms.

The satellites of Jupiter form a miniature planetary system of their own. The four largest satellites are similar in size to Mercury and the Moon but differ significantly in their chemical compositions and surface features.

The satellites of Saturn, Uranus, and Neptune are likewise of great interest in the study of the solar system but are less well known than the satellites of Jupiter.

References

-
- ANONYMOUS, 1989. *Voyager Fact Sheet; Neptune Encounter*. Jet Propulsion Laboratory, Pasadena, CA.
- CAMERON, A. G. W., 1978. Physics of the primitive solar accretion disk. *Moon Planets*, **18**:5-40.
- CAMERON, A. G. W., and M. R. PINE, 1973. Numerical models of the primitive solar nebula. *Icarus*, **18**:377-406.
- CARR, M. H., R. S. SAUNDERS, R. G. STROM, and D. E. WILHELMS, 1984. *The Geology of the Terrestrial Planets*. NASA SP-469, 317 pp.
- GLASS, B. P., 1982. *Introduction to Planetary Geology*. Cambridge University Press, Cambridge, England, 469 pp.
- GREELEY, R., 1985. *Planetary Landscapes*. Allen and Unwin, London, 265 pp.
- HAMBLIN, W. K., and E. H. CHRISTIANSEN, 1990. *Exploring the Planets*. Macmillan, New York, 449 pp.
- HUNT, G., and P. MOORE, 1981. *Jupiter*. Rand McNally, New York, 96 pp.
- LEWIS, J. S., 1974. The chemistry of the solar system. *Sci. Amer.*, **230**(3):51-65.
- MEHLIN, T. G., 1968. *Astronomy and the Origin of the Earth*, Brown Co., Dubuque, IA, 131 pp.
- MORABITO, L. A., S. P. SYNNOTT, P. N. KUPFERMAN, and S. A. COLLINS, 1979. Discovery of currently active extraterrestrial volcanism. *Science*, **204**:972.
- MURRAY, B., M. C. MALIN, and R. GREELEY, 1981. *Earthlike Planets*. W. H. Freeman, San Francisco, 387 pp.
- PEALE, S. J., P. CASSEN, and R. T. REYNOLDS, 1979. Melting of Io by tidal dissipation. *Science*, **203**:892-894.

Chemical Differentiation of the Earth

The Earth is a highly differentiated planet, and its geological activity continues to produce diversified suites of igneous and sedimentary rocks. Although some of the other terrestrial planets may also have remained active in certain limited and specific ways, the Earth still has “fire in her belly” and is cloaked in envelopes of corrosive water and atmospheric gases.

4.1 Internal Structure of the Earth

The Earth was probably initially molten and differentiated very early in its history into several layers or shells having different chemical compositions. The resulting internal structure of the Earth has been determined by seismologists based on the reflection and refraction of compressional (P) and shear (S) seismic waves. On the basis of these results, the interior of the Earth has been divided into the *core*, the *mantle*, and the *crust*, as shown in Figure 4.1. The densities of these major interior units of the Earth range from 2.8 g/cm^3 for rocks in the crust to more than 12 g/cm^3 for the core (Bullen, 1963). The increase of the density and of the velocities of seismic waves with depth is caused both by changes in the chemical composition and by the recrystallization of minerals into more closely packed structures. Figure 4.1 shows that the seismic velocities and densities have two major discontinuities marking the boundaries between the crust and mantle and between the mantle and core. The crust–mantle boundary, located at a depth of

about 40 km under the continents, is known as the Mohorovicic discontinuity or “Moho,” whereas the mantle–core boundary, at a depth of 2883 km, is referred to as the Wiechert–Gutenberg discontinuity, and both are named after eminent seismologists. There are additional, but more subtle, transition regions within the Earth caused by other important changes in its physical properties. Table 4.1 contains a summary of the physical properties of the Earth.

The mantle of the Earth has been subdivided into three parts based on the presence of boundaries at depths of 413 and 984 km. The *upper mantle*, between the Moho and the boundary at about 400 km, is probably heterogeneous because of the formation of magma by partial melting. Xenoliths of ultramafic rocks derived from this region indicate that the upper mantle is composed of olivine, pyroxene, and garnet with lesser amounts of spinel, amphibole, and phlogopite. The *transition zone*, located between depths of about 400 and 1000 km, is a region of pressure-induced phase transformations of the orthosilicates of Fe and Mg from the structure of olivine to that of spinel. The *lower mantle*, below a depth of about 1000 km, is probably homogeneous and may be richer in Fe than the upper mantle (Henderson, 1982).

The chemical composition of the mantle is difficult to determine with certainty because it is inaccessible and heterogeneous. Nevertheless, ultramafic xenoliths, as well as the stony meteorites, have provided useful clues. In addition, large masses of alpine-type peridotite may have originated from the upper mantle at convergent

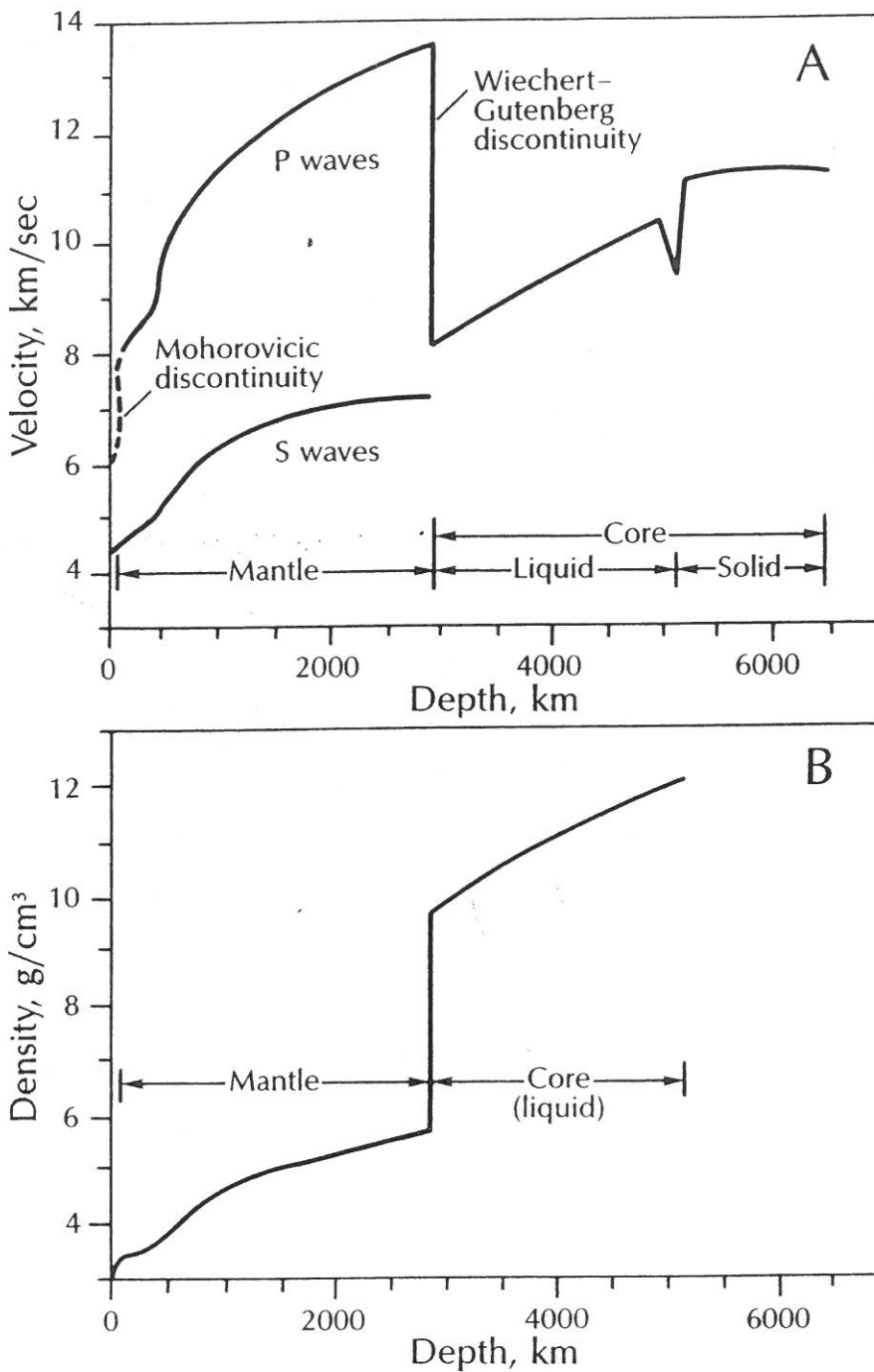


Figure 4.1 A: Variation of seismic velocities with depth in the Earth. The velocity of P waves increases abruptly at the base of the crust (Mohorovicic discontinuity or Moho) from about 6 km/sec to nearly 8 km/sec. It increases with depth in the mantle but drops sharply again at the mantle-core boundary. A third discontinuity in the P-wave velocities within the core marks the transition from the liquid outer core to the solid inner core. The velocity of S waves also increases at the Moho and continues to rise with depth in the mantle. However, S waves do not penetrate the mantle-core boundary, which indicates that the outer core is liquid.

B: The density of rocks rises abruptly at the Moho and continues to increase with depth in the mantle. At the mantle-core boundary the density rises sharply from about 6 g/cm³ to nearly 10 g/cm³, and then continues to increase to values in excess of 12 g/cm³ at the boundary between the outer and inner core. The variation of these physical properties leads to the conclusion that the mantle is solid and is composed primarily of silicates and oxides of Mg and Fe. The core consists of an alloy of Fe, Ni, and other siderophile elements and is liquid except for the inner part which is solid (after Bullen, 1963).

plate boundaries. Estimates of the chemical composition of the mantle must meet certain geophysical requirements regarding density, seismic velocities, and heat production by the decay of U, Th, and K. In addition, the mantle must be capable of forming the major types of

basaltic magmas by partial melting under the physical conditions likely to prevail in that region of the Earth.

These requirements are generally satisfied by a rock called *pyrolite* invented by Ringwood (1966) by combining peridotite and basalt in the ratio of 3.

Table 4.1 Physical Dimensions of the Earth Including the Continental Crust

	Thickness, km	Volume, 10^{27} cm^3	Average density, g/cm^3	Mass, 10^{27} g	Mass, %
Whole Earth	6371 ^a	1.083	5.52	5.976	100
Core	3471 ^a	0.175	10.7	1.876	31.5
Mantle	2883	0.899	4.5	4.075	68.1
Crust ^b	40	0.008 42	2.8	0.023 6	0.4
Hydrosphere	3.8 (av.)	0.001 37	1.03	0.001 41	0.024
Atmosphere	—	—	—	0.000 005	0.000 09

^aRadius.^bContinental crust.

SOURCE: Parker (1967) and Taylor and McLennan (1985).

Table 4.2 Estimates of the Chemical Composition of the Mantle of the Earth

	Sample 1 ^a	Sample 2 ^b	Sample 3 ^c
SiO ₂	45.2	48.1	45.0
MgO	37.5	31.1	39.0
FeO	8.0	12.7	8.0
Al ₂ O ₃	3.5	3.1	3.5
CaO	3.1	2.3	3.25
Na ₂ O	0.57	1.1	0.28
Cr ₂ O ₃	0.43	0.55	0.41
MnO	0.14	0.42	0.11
P ₂ O ₅	0.06	0.34	—
K ₂ O	0.13	0.12	0.04
TiO ₂	0.17	0.12	0.09
NiO	—	—	0.25
Sum	98.8	99.95	99.93

^aPyrolite (Ringwood, 1966).^bMantle plus crust based on meteorites (Mason, 1966).^cUndepleted mantle based on lherzolites (Hutchison, 1974).

to 1. The resulting chemical composition of the mantle is similar to one proposed by Mason (1966), which was based on meteorites, and also resembles the estimate made by Hutchison (1974), which was derived from ultramafic lherzolite inclusions in igneous rocks. The estimates of the chemical composition of the mantle are compiled in Table 4.2.

The great interest by the scientific community in the chemical composition of the mantle and in the Moho caused one of the more colorful episodes in the history of science. In the course of a gathering of some members of the American Miscellaneous Society (AMSOC) in Washington, D.C., chaired by Professor Harry Hess of Princeton University, someone casually suggested that a hole should be drilled through the oceanic crust to find out what causes the Moho. The idea ignited the enthusiastic support of the group, and a proposal was promptly submitted to the National Science Foundation to determine the feasibility of this idea. Thus began the so-called *Mohole Project*, which received much attention in the popular press but never achieved its objective. Nevertheless, engineering studies were made with support from the National Science Foundation, a drilling ship was outfitted, and some test holes were drilled. These tests demonstrated that it was indeed possible to drill in deep water from a ship positioned over the selected site. Eventually AMSOC disbanded, but the equipment was taken over by the Deep-Sea Drilling Program, which has been exploring the history of the ocean basins by drilling first from the *Glomar Challenger* and later from the *Glomar Explorer*. The AMSOC gave up the quest to drill to the Moho partly because it became apparent that this important boundary is actually exposed in some deep-sea trenches and that rocks from the

upper mantle could be, and in fact had been, recovered by dredging.

4.2 The Continental Crust: Major Elements

The crust of the Earth is important because it contains all of the natural resources that sustain us. It includes the *atmosphere*, *hydrosphere*, and *biosphere*, as well as part of the *lithosphere*. The term *lithosphere* is now defined as the rigid outer portion of the Earth consisting of the crust and upper mantle in contrast to the underlying *asthenosphere*, which deforms plastically in response to tectonic stress. The study of the chemical composition of the *continental* crust, and of the different types of rocks of which it is composed, has been a major objective of geochemistry (Wedepohl, 1969; Taylor and McLennan, 1985).

The crust is the outer shell of the Earth, which lies above the mantle. It not only makes up the continents but also occurs under the oceans. The *oceanic* crust is only 5–8 km thick and differs from the continental crust in chemical composition and origin. The continental crust is composed primarily of igneous and metamorphic rocks. Metamorphic rocks are concentrated in orogenic belts, but the distinction between igneous and metamorphic rocks is not always obvious because most of the igneous rocks in the continental crust have been metamorphosed. Sedimentary and volcanic rocks form at the surface of the Earth and therefore tend to cover the underlying igneous and metamorphic rocks. Sedimentary and volcanic rocks may also become folded into elongated masses by compression of tectonic basins in which they were originally deposited. Clarke and Washington (1924) estimated that the continental crust consists of 95% igneous and metamorphic rocks and 5% sedimentary rocks. The latter include 4% shale, 0.75% sandstone, and 0.25% limestone. Evidently, sedimentary rocks make up only a minor portion of the continental crust,

but their occurrence at the surface of the continents enhances their importance.

The chemical composition of the continental crust has been estimated by (1) averaging large numbers of chemical analyses, (2) combining chemical analyses of different rock types weighted in terms of their abundances, (3) analyzing sediment derived from the continent, (4) combining the compositions of acidic and mafic rocks in varying proportions, and (5) by modeling. The results of these different methods are surprisingly similar as indicated in Table 4.3.

Clarke and Washington (1924) estimated the chemical composition of the crust not only by averaging a large number of chemical analyses of igneous rocks from all continents and from the ocean basins, but also by combining the average chemical composition of igneous rocks with those of shale, sandstone, and limestone in accordance with their observed abundances. The results in columns 1 and 2 of Table 4.3 are very similar. An enormous amount of work was required to collect and analyze the well over 5000 rock samples on which the estimate in column 1 is based. Therefore, V. M. Goldschmidt decided in the early 1930s to analyze the clay-size fraction of till in southern Norway because, he argued, glacial sediment of Pleistocene age was produced by mechanical erosion of bedrock in Scandinavia with little chemical weathering. In addition, transport at the base of the ice sheet and subsequent deposition by melt-water caused glacial clay to be well mixed, making it a representative sample of the rocks in the path of the ice sheet. The average chemical composition of 77 samples of glacial clay from southern Norway (column 3, Table 4.3) is, in fact, quite similar to the estimates of Clarke and Washington. We note, however, that the concentrations of CaO and Na₂O of the glacial clay are somewhat *lower* than their values in columns 1 and 2, presumably because these elements were partially lost from the clay by leaching. In addition, the glacial clays have a lower TiO₂ content than the crustal averages of Clarke and Washington, which may be a regional characteristic of the rocks of Scandinavia.

Table 4.3 Estimates of the Average Chemical Composition of the Continental Crust in Weight Percents

	1 ^a	2 ^b	3 ^c	4 ^d	5 ^e	6 ^f	7 ^g	8 ^h
SiO ₂	59.12	59.07	59.19	60.06	59.4	59.3	57.3	68.4
TiO ₂	1.05	1.03	0.79	0.90	1.2	0.7	0.9	0.4
Al ₂ O ₃	15.34	15.22	15.82	15.52	15.6	15.0	15.9	14.8
Fe ₂ O ₃	3.08	3.10	3.41	3.55	2.3	2.4	—	1.3
FeO	3.80	3.71	3.58	4.06	5.0	5.6	9.1	3.2
MnO	0.12	0.11	0.11	0.21	0.1	0.1	—	—
MgO	3.49	3.45	3.30	3.56	4.2	4.9	5.3	1.7
CaO	5.08	5.10	3.07	5.62	6.6	7.2	7.4	3.4
Na ₂ O	3.84	3.71	2.05	3.28	3.1	2.5	3.1	3.1
K ₂ O	3.13	3.11	3.93	2.88	2.3	2.1	1.1	3.6
P ₂ O ₅	0.30	0.30	0.22	0.36	0.2	0.2	—	0.1
CO ₂	—	0.35	0.54	—	—	—	—	—
H ₂ O	1.15	1.30	3.02	—	—	—	—	—
Sum	99.50	99.56	99.03	100.00	100.0	100.0	100.1	100.0

^aClarke and Washington (1924) based on the average of 5159 analyses of igneous rocks from all continents and the oceans.

^bClarke and Washington (1924) based on 95% igneous rocks, 4% shale, 0.75% sandstone, 0.25% limestone.

^cGoldschmidt (1954) based on 77 analyses of glacial clay from southern Norway.

^dDaly (1914) based on 1 : 1 mixture of average granite and basalt.

^ePoldervaart (1955), based on the average of young folded belts and continental shield region shown in Table 4.4.

^fRonov and Yaroshevsky (1976) based on a detailed model like that of Poldervaart (1955).

^gTaylor and McLennan (1985, Table 3.4, No. 10) based on 75% Archean crust and 25% andesite crust.

^hSederholm (1925) based on the Precambrian rocks of Finland.

SOURCE: Parker (1967); Taylor and McLennan (1985).

Columns 4–8 of Table 4.3 contain estimates of the chemical composition of the continental crust derived by various methods. Daly (1914) estimated its composition by combining analyses of granite and basalt in equal proportions (column 4, Table 4.3) because these rock types were thought to originate from fundamental magmas of granitic and basaltic compositions. Poldervaart (1955) constructed a detailed model by dividing the crust into the *continental shields*, *young folded belts*, the *suboceanic region*, and the *deep oceanic region*. He assigned each region certain lithologic compositions (indicated in Table 4.4) and combined the chemical compositions of the different rock types according to their abundances. Column 5 of Table 4.3 contains his estimate of the chemical composition of the continental

crust as a whole. Poldervaart's estimates of the chemical composition of each of the four structural units are shown separately in Table 4.4. These results illustrate the differences in the chemical composition of the *continental crust* (continental shield + young folded belts) and the *oceanic crust* (deep oceanic region). It is evident that the oceanic crust has higher average concentrations of Fe₂O₃ + FeO, MgO, CaO, MnO, P₂O₅, and TiO₂ and lower concentrations of SiO₂, Al₂O₃, Na₂O, and K₂O than the continental crust (column 5, Table 4.4). These differences arise because the continental crust is composed primarily of granitic rocks (granodiorite?), whereas the oceanic crust was assumed by Poldervaart (1955) to consist largely of olivine basalt. However, the study of *ophiolite complexes*,

Table 4.4 Estimates of the Chemical Composition of Four Major Structural Units of the Lithic Crust of the Earth in Weight Percent

	Poldervaart				Ronov and Yaroshevsky
	1 Continental shields ^a	2 Young folded belts ^b	3 Suboceanic regions ^c	4 Deep oceanic ^d	5 Oceanic crust
SiO ₂	59.8	58.4	49.4	46.6	49.4
TiO ₂	1.2	1.1	1.9	2.9	1.4
Al ₂ O ₃	15.5	15.6	15.1	15.0	15.4
Fe ₂ O ₃	2.1	2.8	3.4	3.8	2.7
FeO	5.1	4.8	6.4	8.0	7.6
MnO	0.1	0.2	0.2	0.2	0.3
MgO	4.1	4.3	6.2	7.8	7.6
CaO	6.4	7.2	13.2	11.9	12.5
Na ₂ O	3.1	3.1	2.5	2.5	2.6
K ₂ O	2.4	2.2	1.3	1.0	0.3
P ₂ O ₅	0.2	0.3	0.3	0.3	0.2
Sum	100.0	100.0	100.0	100.1	100.0

^aSedimentary cover ~0.5 km: 41% shale, 43% sandstone, 16% limestone. Igneous rocks vary in composition with depth such that there are 22 km of granodiorite, 3 km of diorite, and 10.5 km of basalt.

^bSedimentary cover ~5 km: 52% shale, 13% sandstone, 22% limestone, 5% greywacke, 6% andesite, 2% rhyolite. Igneous rocks: 22.5 km of granodiorite, 2.7 km of diorite, and 7.3 km of basalt. In addition, 40% of the sediment layer is assumed to be granodiorite based on the outcrop area of granitic batholiths.

^cShelf sediment ~4 km, similar in composition to that of folded mountain belts. In addition: 74% terrigenous mud, 22% coral mud, 4% volcanic mud. Igneous rocks: 4 km of diorite, 2 km of tholeiite, and 5 km of olvine basalt.

^dSediment thickness ~0.3 km: 72% calcareous sands and oozes, 19% red clay, 9% siliceous ooze. Igneous rocks: 5.57 km of olvine basalt.

SOURCE: Poldervaart (1955); Ronov and Yaroshevsky (1976).

summarized by Moores (1982), indicates that the oceanic crust is actually composed of mafic and ultramafic rocks, whose average composition may approach that of basalt, although trace element concentrations have been altered by interaction with heated seawater. Ronov and Yaroshevsky (1976) also modeled the continental and oceanic crust and arrived at compositions that are similar to those of Poldervaart (1955). Their estimate of the chemical composition of the continental crust is listed in column 6 of Table 4.3, whereas column 5 of Table 4.4 contains their estimate for the oceanic crust.

Taylor (1964) revived Daly's method of estimating the chemical composition of the continental crust by demonstrating that the average concentrations of rare earth elements (REEs) in sedimentary

rocks can be duplicated by combining chemical analyses of mafic and felsic igneous rocks in the proportions 1:5. The resulting chemical composition resembles that of diorite or andesite, which is why this crustal model is generally referred to as the *andesite* model. Subsequently, Taylor and McLennan (1985) proposed that the continental crust consists of 75% average Archean rocks and 25% andesite crust. The resulting composition is shown in column 7 of Table 4.3. It differs from all other estimates listed in Table 4.3 by having somewhat *lower* concentrations of SiO₂, TiO₂, Na₂O, and K₂O and *higher* concentrations of Al₂O₃, Fe as FeO, MgO, and CaO. Accordingly, the chemical composition of the continental crust proposed by Taylor and McLennan (1985) is somewhat more

mafic than those of their predecessors. However, it does meet the following important constraints.

1. It satisfies the observed rate of heat flow based on the decay of U, Th, and K.
2. It is capable of generating the more highly differentiated granodiorites of the upper crust by partial melting.
3. It restricts crustal growth by andesitic island-arc volcanism to post-Archean time.
4. It recognizes that 75% of the continental crust is composed of rocks that are more than 2500 million years old, which did not necessarily form by the same tectonic-magmatic processes that became important in post-Archean time.

In conclusion, we note that the chemical composition of the continental crust of the Earth is very different from that of the solar nebula and stony meteorites. The nine most abundant elements and their average concentrations in the continental crust are:

	Wt. %		Wt. %
O	45.5	Mg	3.2
Si	26.8	Na	2.3
Al	8.40	K	0.90
Fe	7.06	Ti	0.5
Ca	5.3		

All of the remaining elements make up only a very small fraction of the crust of the Earth.

4.3 Differentiation of Igneous and Sedimentary Rocks

The chemical compositions of igneous rocks vary widely because of geochemical differentiation that takes place during their formation. The differentiation starts during magma formation by partial melting of rocks in the lower crust or upper mantle. The chemical composition of the resulting magma depends on the composition of the source rocks and

on the extent of melting, which is controlled by the pressure and temperature at the source. The composition of magmas may be modified subsequently by assimilation of country rocks or by mixing with magmas derived from different sources. The crystallization of magmas depends on their chemical compositions and on the physical conditions in the magma chamber. The rocks produced by fractional crystallization of magma may vary widely in their mineral composition from ultramafic cumulates of early-formed ferromagnesian minerals (olivine or pyroxene) to quartz-rich late-stage differentiates.

The most comprehensive compilation of the chemical compositions of the highly diverse igneous rocks can be found in the *Handbook of Geochemistry*, edited by K. H. Wedepohl from 1969 to 1978. The compilation of data in Table 4.5 is based on earlier compilations by Turekian and Wedepohl (1961) and Vinogradov (1962). The data are grouped into ultramafic rocks, basalt, high-Ca granite, and low-Ca granite and therefore represent most of the compositional spectrum of igneous rocks. The category "basalt" includes both volcanic and plutonic rocks of basaltic composition, whereas the "high-Ca granites" represent igneous rocks of intermediate composition, which may not actually be *granites* in the strict sense of that term.

The sedimentary rocks are just as highly diversified in their chemical compositions as igneous rocks. However, the processes that cause this diversification operate on the *surface* of the Earth rather than at depth and include *weathering*, *transport*, *deposition*, and *lithification*. The study of these processes encompasses a major portion of the subject of geochemistry and will occupy the remainder of this book.

Sedimentary rocks can be divided into two groups depending on whether they are composed of mineral and rock particles of preexisting rocks or whether they precipitated from aqueous solution. This division is not completely justified because clastic sedimentary rocks may contain chemically precipitated mineral cements, whereas the chemical precipitates may contain a component of detrital sediment. Moreover, the chemical compositions of rocks in both groups are modified

Table 4.5 Chemical Composition of Igneous and Sedimentary Rocks (in parts per million unless otherwise indicated)

<i>Element, Z</i>	<i>Ultramafic^a</i>	<i>Basalt^a</i>	<i>High-Ca granites^b</i>	<i>Low-Ca granites^b</i>	<i>Shale^b</i>	<i>Sandstone^b</i>	<i>Carbonate rocks^b</i>	<i>Deep-sea clay^b</i>
3 Li	0.5	16	24	40	66	15	5	57
4 Be	0.2	0.7	2	3	3	—	—	2.6
5 B	2	5	9	10	100	35	20	230
9 F	100	385	520	850	740	270	330	1300
11 Na (%)	0.49	1.87	2.84	2.58	0.96	0.33	0.04	4
12 Mg (%)	23.2	4.55	0.94	0.16	1.50	0.70	4.70	2.10
13 Al (%)	1.2	8.28	8.20	7.20	8	2.50	0.42	8.40
14 Si (%)	19.8	23.5	31.40	34.70	7.30 ^e	36.80	2.40	25
15 P	195	1130	920	600	700	170	400	1500
16 S	200	300	300	300	2400	240	1200	1300
17 Cl	45	55	130	200	180	10	150	21000
19 K (%)	0.017	0.83	2.52	4.20	2.66	1.07	0.27	2.50
20 Ca (%)	1.6	7.2	2.53	0.51	2.21	3.91	30.23	2.90
21 Sc	10	27	14	7	13	1	1	19
22 Ti	300	11400	3400	1200	4600	1500	400	4600
23 V	40	225	88	44	130	20	20	120
24 Cr	1800	185	22	4.1	90	35	11	90
25 Mn	1560	1750	540	390	850	—	1100	6700
26 Fe (%)	9.64	8.60	2.96	1.42	4.72	0.98	0.33	6.50
27 Co	175	47	7	1	19	0.3	0.1	74
28 Ni	2000	145	15	4.5	68	2	20	225
29 Cu	15	94	30	10	45	—	4	250
30 Zn	40	118	60	39	95	16	20	165
31 Ga	1.8	18	17	17	19	12	4	20
32 Ge	1.3	1.4	1.3	1.3	1.6	0.8	0.2	2
33 As	0.8	2.2	1.9	1.5	13	1	1	13
34 Se	0.05	0.05	0.05	0.05	0.6	0.05	0.08	0.17
35 Br	0.8	3.3	4.5	1.3	4	1	6.2	70
37 Rb	1.1	38	110	170	140	60	3	100
38 Sr	5.5	452	440	100	300	20	610	180
39 Y	—	21	35	40	26	40	30	90
40 Zr	38	120	140	175	160	220	19	150
41 Nb	9	20	20	21	11	—	0.3	14
42 Mo	0.3	1.5	1	1.3	2.6	0.2	0.4	27
47 Ag	0.05	0.11	0.051	0.037	0.07	0.01	0.01	0.11
48 Cd	0.05	0.21	0.13	0.13	0.3	—	0.035	0.42
49 In	0.012	0.22	—	0.26	0.1	—	—	0.08
50 Sn	0.5	1.5	1.5	3	6	0.1	0.1	1.5
51 Sb	0.1	0.6	0.2	0.2	1.5	0.01	0.2	1
53 I	0.3	0.5	0.5	0.5	2.2	1.7	1.2	0.05
55 Cs	0.1	1.1	2	4	5	0.1	0.1	6
56 Ba	0.7	315	420	840	580	10	10	2300
57 La	1.3 ^c	6.1 ^d	45	55	92	30	1	115
58 Ce	3.5 ^c	16 ^d	81	92	59	92	11.5	345
59 Pr	0.49 ^c	2.7 ^d	7.7	8.8	5.6	8.8	1.1	33

Table 4.5 (continued)

Element, Z	Ultramafic ^a	Basalt ^a	High-Ca granites ^b	Low-Ca granites ^b	Shale ^b	Sandstone ^b	Carbonate rocks ^b	Deep-sea clay ^b
60 Nd	1.9 ^c	14 ^d	33	37	24	37	4.7	140
62 Sm	0.42 ^c	4.3 ^d	8.8	10	6.4	10	1.3	38
63 Eu	0.14 ^c	1.5 ^d	1.4	1.6	1	1.6	0.2	6
64 Gd	0.54 ^c	6.2 ^d	8.8	10	6.4	10	1.3	38
65 Tb	0.12 ^c	1.1 ^d	1.4	1.6	1	1.6	0.2	6
66 Dy	0.77 ^c	5.9 ^d	6.3	7.2	4.6	7.2	0.9	27
67 Ho	0.12 ^c	1.4 ^d	1.8	2	1.2	2	0.3	7.5
68 Er	0.30 ^c	3.6 ^d	3.5	4	2.5	4	0.5	15
69 Tm	0.041 ^c	0.60 ^d	0.3	0.3	0.2	0.3	0.04	1.2
70 Yb	0.38 ^c	3.2 ^d	3.5	4	2.6	4	0.5	15
71 Lu	0.036 ^c	0.55 ^d	1.1	1.2	0.7	1.2	0.2	4.5
72 Hf	0.4	1.5	2.3	3.9	2.8	3.9	0.3	4.1
73 Ta	0.5	0.8	3.6	4.2	0.8	0.01	0.01	0.1
74 W	0.5	0.9	1.3	2.2	1.8	1.5	0.6	1
79 Au	0.006	0.004	0.004	0.004	—	—	—	—
80 Hg	0.01	0.09	0.08	0.08	0.4	0.03	0.04	0.1
81 Tl	0.04	0.21	0.72	2.3	1.4	0.82	0.01	0.8
82 Pb	0.5	7	15	19	20	7	9	80
90 Th	0.0045	3.5	8.5	17	12	1.7	1.7	7
92 U	0.002	0.75	3	3	3.7	0.45	2.2	1.3

^aAverage of Turekian and Wedepohl (1961) and Vinogradov (1962).

^bTurekian and Wedepohl (1961).

^cCalculated from data listed by Herrmann (1970).

^dAverage values calculated by Hermann (1970).

^eKrauskopf (1979) listed a value of 23.8%.

by ion exchange processes associated with electrical surface charges of mineral grains regardless of whether they are detrital or formed as chemical precipitates.

The compilation of data in Table 4.5 includes two rock types that are predominantly detrital (shale and sandstone), one that is predominantly precipitated (carbonate rocks), and deep-sea clay, which is a mixture of detrital grains and chemical precipitates. The selection of these rock types has an additional virtue because it includes rocks that form in shallow marine basins in the vicinity of continents as well as sediment deposited in deep ocean basins far from land.

The apparent geochemical differentiation indicated by these data reflects the way in which geological processes operating on the surface of

the Earth "sort" the elements on the basis of their chemical properties. We can think of the surface environment of the Earth as a giant *machine* that processes igneous and metamorphic rocks into a wide variety of sedimentary rocks. The products of this machine are highly diversified because the chemical elements, and the minerals they form, respond differently to the treatment they experience as they pass through the machine.

The representation of geological processes operating on the surface of the Earth as a machine is helpful because it emphasizes the *coherence* of these processes and because it promotes a *global* view of the geochemistry of the Earth's surface. We return to this theme in Part V of this book, where we consider the geochemical cycles of selected elements (Chapter 22).

4.4 Differentiation of the Hydrosphere

The hydrosphere consists of a number of reservoirs of water that are connected by means of the hydrologic cycle. Table 4.6 indicates that the oceans are by far the largest reservoirs of water with 97.25% of the total volume, followed by ice sheets and glaciers (2.05%) and deep groundwater (0.38%). That leaves a very small fraction of the water in the hydrosphere in shallow groundwater (0.30%), lakes (0.01%), and rivers (0.0001%) where it is accessible to humans for municipal and industrial use (see also Chapter 20).

When igneous, metamorphic, or sedimentary rocks come in contact with water at or near the surface of the Earth, different kinds of chemical reactions occur, which collectively constitute *chemical weathering* or *water-rock interaction*. The outcome of these reactions depends not only on the chemical and physical conditions at the site but also on the properties of the minerals. Minerals vary widely in their susceptibility to chemical weathering although most are quite insoluble in water. Therefore, the chemical elements do *not* enter the aqueous phase in the same proportions in which they occur in the rocks of the continental crust. As a result, the chemical composition of surface water or groundwater differs from that of the rocks of the upper continental crust in ways that reflect the geochemical properties of the elements and of the minerals they form. Whitfield and Turner (1979) actually expressed these differences in terms of partition coefficients (water/upper crust) and showed that they are related to the ionic character of the metal-oxygen bonds in the minerals.

Once an element has entered the hydrosphere, it is subjected to other kinds of processes that may affect its concentration. For example, some ions are selectively adsorbed on the charged surfaces of clay minerals or particles of oxides and hydroxides of Fe, Mn, and Al. Other elements may enter the biosphere as nutrients and become associated with organisms and biogenic carbon compounds. The noble gases are released into the atmosphere, whereas oxygen, carbon dioxide, and

Table 4.6 Inventory of Water in the Hydrosphere

<i>Reservoir</i>	<i>Volume, 10⁶ km³</i>	<i>Percent, of total</i>
Oceans	1370	97.25
Ice sheets and glaciers	29	2.05
Deep groundwater (750–4000 m)	5.3	0.38
Shallow groundwater (<750 m)	4.2	0.30
Lakes	0.125	0.01
Soil moisture	0.065	0.005
Atmosphere ^a	0.013	0.001
Rivers	0.001 7	0.000 1
Biosphere	0.000 6	0.000 04
Total	1408.7	100

^aLiquid equivalent of water vapor.

SOURCE: Berner and Berner (1987).

nitrogen of the atmosphere dissolve in the water. Therefore, the chemical composition of water varies widely and reflects not only the mineral composition of the rocks it has interacted with, but is also affected by the geochemical environment, which is determined by climate, topography, vegetation, and by the possible discharge of industrial or municipal waste. These matters are considered in much greater detail in Part V.

Streams ultimately transport the elements that dissolve in the water to the oceans where they reside for varying periods of time. The geochemical processes operating in the oceans *selectively* remove elements from solution in such a way that seawater is *not* simply average river water that has been concentrated by evaporation. This statement is supported by inspection of the average concentrations of the elements in streams and in the oceans (Table 4.7). The fifth column in Table 4.7 contains enrichment factors calculated by dividing the concentration of each element in the oceans by its concentration in average river water. The resulting enrichment factors vary widely from 3350 for Br to about 0.0006 for Th. Evidently, geochemical processes in the oceans are changing its

Table 4.7 Average Composition of Water in Streams and in the Oceans in micrograms per gram

<i>Element</i>	<i>Classification^a</i>	<i>Stream water</i>	<i>Seawater</i>	<i>Seawater enrichment</i>	<i>MORT^b</i>
Li	I	3×10^{-3}	1.7×10^{-1}	56.7	2.5×10^6
Be	IV	1×10^{-5}	2×10^{-7}	0.02	6.3×10^1
B	I	1×10^{-2}	4.5	450	1.6×10^7
F	I	1×10^{-3}	1.3	1300	7.9×10^5
Na	I	6.3	1.08×10^4	1714	2.0×10^8
Mg	I	4.1	1.29×10^3	315	5.0×10^7
Al	IV	5×10^{-2}	8×10^{-4}	0.016	7.0
Si	II	6.5	2.8	0.43	7.9×10^3
P	II	2×10^{-2}	7.1×10^{-2}	3.6	4.0×10^4
S	I	3.7	9.0×10^2	243	5.0×10^8
Cl	I	7.8	1.95×10^4	2500	6.3×10^8
K	I	2.3	3.99×10^2	173	1.3×10^7
Ca	I	15	4.13×10^2	27.5	1.3×10^6
Sc	IV	4×10^{-6}	6.7×10^{-7}	0.17	2.5×10^1
Ti	IV	3×10^{-3}	$<9.6 \times 10^{-4}$	0.32	$<1.6 \times 10^2$
V	IV	9×10^{-4}	1.2×10^{-3}	1.3	7.9×10^3
Cr	IV	1×10^{-3}	2×10^{-4}	0.2	1.6×10^3
Mn	III	7×10^{-3}	3×10^{-4}	0.04	3.2×10^1
Fe	IV	4×10^{-2}	6×10^{-5}	0.0015	6.9×10^{-1}
Co	III	1×10^{-4}	2×10^{-6}	0.02	2.0×10^1
Ni	III	3×10^{-4}	5×10^{-4}	1.7	1.6×10^3
Cu	III	7×10^{-3}	3×10^{-4}	0.04	1.0×10^3
Zn	III	2×10^{-2}	4×10^{-4}	0.02	1.3×10^3
Ga	IV	9×10^{-5}	2×10^{-5}	0.2	7.9×10^2
Ge	IV	5×10^{-6}	5×10^{-6}	1	2.0×10^3
As	IV	2×10^{-3}	1.7×10^{-3}	0.85	1.0×10^5
Se	III	6×10^{-5}	1.3×10^{-4}	2.2	6.3×10^5
Br	I	2×10^{-2}	6.7×10^1	3350	7.9×10^8
Rb	I	1×10^{-3}	1.2×10^{-1}	120	7.9×10^5
Sr	I	7×10^{-2}	7.6	109	5.0×10^6
Y	III	4×10^{-5}	7×10^{-6}	0.18	1.3×10^2
Zr	IV	—	3×10^{-5}	—	1.6×10^2
Nb	IV	—	$<5 \times 10^{-6}$	—	$<2.5 \times 10^2$
Mo	I	6×10^{-4}	1.1×10^{-2}	18.3	3.2×10^5
Ag	III	3×10^{-4}	2.7×10^{-6}	0.009	2.0×10^4
Cd	IV	1×10^{-5}	8×10^{-5}	8	7.9×10^4
In	IV	—	1×10^{-7}	—	1.0×10^3
Sn	IV	4×10^{-5}	5×10^{-7}	0.013	1.3×10^2
Sb	III	7×10^{-5}	1.5×10^{-4}	2.1	1.3×10^5
I	I	7×10^{-3}	5.6×10^{-2}	8	$<4.0 \times 10^6$
Cs	I	2×10^{-5}	2.9×10^{-4}	14.5	4.0×10^4
Ba	III	2×10^{-2}	1.4×10^{-2}	0.7	5.0×10^3
La	III	4.8×10^{-5}	4.5×10^{-6}	0.094	7.9×10^1
Ce	III	7.9×10^{-5}	3.5×10^{-6}	0.044	3.2×10^1

Table 4.7 (continued)

Element	Classification ^a	Stream water	Seawater	Seawater enrichment	MORT ^b
Pr	III	7.3×10^{-6}	1.0×10^{-6}	0.14	7.9×10^1
Nd	III	3.8×10^{-5}	4.2×10^{-6}	0.11	7.9×10^1
Sm	III	7.8×10^{-6}	8.0×10^{-7}	0.10	7.9×10^1
Eu	III	1.5×10^{-6}	1.5×10^{-7}	0.10	6.3×10^1
Gd	III	8.5×10^{-6}	1.0×10^{-6}	0.11	1.0×10^2
Tb	III	1.2×10^{-6}	1.7×10^{-7}	0.14	1.0×10^2
Dy	III	7.2×10^{-6}	1.1×10^{-6}	0.15	1.0×10^2
Ho	III	1.4×10^{-6}	2.8×10^{-7}	0.20	1.3×10^2
Er	III	4.2×10^{-6}	9.2×10^{-7}	0.22	1.6×10^2
Tm	III	6.1×10^{-7}	1.3×10^{-7}	0.21	1.6×10^2
Yb	IV	3.6×10^{-6}	9.0×10^{-7}	0.25	2.0×10^2
Lu	IV	6.4×10^{-7}	1.4×10^{-7}	0.22	2.0×10^2
Hf	IV	—	$<7 \times 10^{-6}$	—	$<1.3 \times 10^3$
Ta	IV	—	$<2.5 \times 10^{-6}$	—	$<2.0 \times 10^3$
W	IV	3×10^{-5}	1×10^{-4}	3.3	7.9×10^4
Re	IV	—	4×10^{-6}	—	3.2×10^6
Au	III	2×10^{-6}	4.9×10^{-6}	2.5	1.6×10^6
Hg	III	7×10^{-5}	1×10^{-6}	0.14	7.9×10^3
Tl	IV	—	1×10^{-5}	—	6.3×10^3
Pb	III	1×10^{-3}	2×10^{-6}	0.002	5.0×10^1
Bi	IV	—	2×10^{-5}	—	2.5×10^4
Th	IV	$<1 \times 10^{-4}$	6×10^{-8}	~ 0.0006	3.4
U	I	4×10^{-5}	3.1×10^{-3}	2.7	1×10^6

^aI. Conservative element whose concentration is directly related to the salinity of seawater.

II. Nonconservative element whose concentration varies with depth or regionally within the oceans, or both, generally because of involvement in biological activity.

III. Nonconservative element whose concentration varies irregularly and is not related to salinity, depth, or geographic factors.

IV. Unclassified, but probably nonconservative.

^bMean oceanic residence time in years.

SOURCE: Taylor and McLennan (1985).

chemical composition in comparison with river water and thereby contribute to the geochemical differentiation of the hydrosphere.

The eventual fate of all elements and compounds dissolved in the ocean is to be removed from it. Most elements are incorporated into the sediment that is accumulating at the bottom of the oceans, but a few elements escape from the ocean into the atmosphere, whose composition is summarized in Table 4.8. These changes in residence are part of the *migration* of elements on the surface of the Earth and contribute to the operation of *geochemical cycles* (see Chapter 22). Every

element is moved from one reservoir to the next by geological, geochemical, or biological processes operating on the surface of the Earth. This is the geochemical machine we spoke of earlier.

The dissolved constituents in the oceans can be divided into the *conservative* (I in Table 4.7) and *nonconservative* groups (II and III in Table 4.7). The conservative elements occur in *constant proportions* throughout the oceans, although their *concentrations* may vary because of dilution or evaporative concentration. This group includes the major elements and complex anions—Na, K, Mg, Ca, Cl, sulfate, and borate. The concentrations

Table 4.8 Chemical Composition of Dry Air

Constituent	Concentration by Volume	
	%	ppm
N ₂	78.084	—
O ₂	20.946	—
CO ₂	0.033	—
Ar	0.934	—
Ne	—	18.18
He	—	5.24
Kr	—	1.14
Xe	—	0.087
H ₂	—	0.5
CH ₄	—	2
N ₂ O	—	0.5

Data from the *CRC Handbook of Chemistry and Physics* (Weast et al., 1986).

of the nonconservative elements vary with depth as well as regionally within the oceans, and their concentration ratios with chloride are *not* constant. The nonconservative elements in seawater include most of the trace elements along with dissolved nitrate, bicarbonate, silicic acid, phosphate, and dissolved oxygen. The concentrations of many nonconservative constituents vary with depth because they are involved in the biological activity of the oceans. As a result, they have low concentrations in the surface layer of the oceans where most of the biological activity is concentrated. When the organisms die, their bodies sink and decompose, thereby returning nutrients to the water. Consequently, deep ocean water is enriched in nutrients compared to surface water.

The conservative constituents have large enrichment factors, indicating that they are *unreactive* and therefore become concentrated in seawater compared to river water. The average enrichment factor of the major (conservative) constituents of seawater is 775. These elements are generally joined by their congeners, many of which are trace elements. For example, the alkali metals, alkaline earths (except Be and Ba), and halogens all have higher concentrations in seawater than in

river water. Their average enrichment factors in the oceans are

Alkali metals	416	(14.5–1714)
Alkaline earths (except Be and Ba)	151	(27.5–315)
Halogens	1790	(8–3350)

In addition, B and S, both of which are major conservative elements, have large enrichment factors indicating that they too tend to accumulate in the oceans. They are followed by P, V, Ni, Ge, Se, Mo, Sb, W, Au, and U, whose enrichment factors are all <20 but >1. Only Mo and U are conservative among the elements in this group.

The enrichment factors of the remaining non-conservative elements are all <1, an indication that they are rapidly removed from seawater by geochemical processes. The concentrations of these elements in seawater are controlled primarily by ion exchange reactions with particulate matter, by ionic substitution in calcium carbonate, calcium phosphate, and amorphous silica, which are in large part biogenic in origin, by direct precipitation caused by evaporation of seawater, and by exchange reactions with volcanic rocks along spreading ridges (Hart and Staudigel, 1982). The concentrations of most elements in seawater are *not* controlled by the solubilities of their compounds.

In contrast to the conservative elements (and a few nonconservative ones), the majority of the nonconservative elements do *not* accumulate in the ocean but are rapidly removed from it by one or several of the geochemical processes mentioned earlier. The adsorption of ions on the charged surfaces of both inorganic and organic particles plays a very important role in this regard and was described by Broecker and Peng (1982) as “the great particulate sweep.” Other important books on the geochemistry of seawater are by Berner and Berner (1987), Holland (1978), Goldberg (1972), and Riley and Chester (1971).

The wide variation of the enrichment factors we have been discussing implies that the unreactive conservative elements remain in the oceanic reservoir much longer than the reactive noncon-

servative elements. This phenomenon is reflected by the *residence time* defined as:

$$t = \frac{A_x}{dX/dt} \quad (4.1)$$

where t is the residence time in years, A_x is the total amount of an element (x) in solution in the oceans, and dX/dt is the average annual input of that element into the oceans. The amount A_x of an element in the oceans is assumed to be constant, which is probably valid for the open ocean but may not apply to the continental shelves and estuaries. The annual input into the oceans can be estimated from the discharge and chemical composition of the major rivers of the Earth. Such estimates are uncertain, however, because both discharge and elemental concentrations of streams vary seasonally and are not known for all rivers with equal certainty (see also Chapter 20). In addition, the runoff of groundwater into the oceans is disregarded because of lack of information. Furthermore, the discharge of industrial and municipal waste water has significantly altered the chemical composition of many rivers. For this reason Taylor and McLennan (1985) estimated the average annual input to the oceans from the rate of deposition and the chemical composition of deep-sea sediment as originally suggested by Li (1982). Accordingly, the mean oceanic residence times (MORT) listed in Table 4.7 were calculated by this method based on sedimentation rates provided by Lisitsyn et al. (1982). The MORTs calculated from the output to deep-sea sediment differ from those obtained from river-input data, but the two sets of results are well correlated.

Actually, the residence time of elements in the oceans was first used to estimate the age of the Earth. The idea was originally suggested in 1715 by Edmund Halley, but nothing was done about it for nearly 200 years. Finally, in 1899 John Joly took up Halley's suggestion and calculated the residence time of Na in the oceans. His result was 90 million years, which is less than half the 200 million years calculated by Taylor and McLennan (1985). Nevertheless, Joly's result was an important milestone in the history of

geology because it contradicted Lord Kelvin's calculations based on the cooling of the Earth, which indicated that its age was less than 40 million years.

The MORTs of the elements in Table 4.7 vary over nine orders of magnitude from 0.69 years for Fe to 7.9×10^8 years for Br. As expected, the conservative elements have long residence times, whereas many nonconservative elements have significantly shorter residence times. The average residence times in the oceans of the *conservative* elements are

	Years
Alkali metals	43.3×10^6
Alkaline earths (except Be and Ba)	18.8×10^6
Halogens	356.2×10^6

The other two major elements (B and S) have residence times of 16×10^6 and 500×10^6 years, respectively.

The lithophile elements have widely different enrichment factors and residence times, whereas a majority of the chalcophile and siderophile elements are depleted in seawater and have short residence times.

Evidently, the oceans play a very important role in the geochemical differentiation of the crust of the Earth by storing some elements and letting others pass rapidly to the sediment accumulating at the bottom of the oceans. The elements that are removed from the oceans in the form of sediment may ultimately reenter the rock cycle and become the input for another pass through the geochemical machine.

4.5 Summary

The Earth differentiated very early in its history into a core, mantle, and crust with characteristic chemical compositions. The core consists of metallic Fe, Ni, and related elements. The mantle is composed primarily of silicates and oxides of Mg and Fe. The chemical composition of the continental crust has been estimated in different ways with generally concordant results. The nine

most abundant chemical elements in the continental crust of the Earth are O, Si, Al, Fe, Ca, Mg, Na, K, and Ti. All other elements together make up only a very small fraction of the continental crust.

The distribution of trace elements among different kinds of igneous rocks depends on their ability to replace major elements in the ionic crystals that form during crystallization of magma. As a result, different kinds of igneous rocks are enriched in specific trace elements, some of which are important industrial metals. Certain kinds of igneous rocks may therefore host ore deposits of these metals.

The chemical compositions of sedimentary rocks are just as diversified as those of the

igneous rocks. They form by chemical weathering of igneous, metamorphic, and sedimentary rocks and by the transport, deposition, and lithification of the resulting products. Many elements become concentrated in deep-sea clay and may reenter the rock cycle when deep-sea sediment melts in subduction zones to form magma.

The oceans play an important role in the chemical differentiation of the crust because some elements accumulate in seawater, whereas others pass through it rapidly. The geological and geochemical processes associated with chemical weathering of minerals, transport of weathering products, and their ultimate deposition in the oceans are the subjects of Part III of this book.

Problems

1. Recalculate the chemical composition of pyrolite (Table 4.2, column 1) in terms of the weight percent concentrations of the elements and rank them in terms of their abundance.

2. Recalculate the concentrations of Si, Al, Fe, Ca, Mg, Na, K, Ti, Mn, and P of shale, sandstone, and carbonate rocks (Table 4.5) in terms of the appropriate oxides.

3. Combine the concentrations calculated in Problem 2 in proportions of 4 parts shale, 0.75 parts sandstone, and 0.25 parts limestone.

4. Compare the results of Problem 3 to the estimates of the average chemical composition of the continental crust (Table 4.3). Take note of discrepancies and similarities and relate them to the geochemical properties of the individual elements.

5. Assess the validity of the hypothesis that the sedimentary rocks (shale, sandstone, and limestone) collectively represent the "weathering crust" on the continents. What additional sources or sinks are needed to adequately describe the redistribution of elements from the continental crust into different kinds of marine sediment?

References

- BERNER, E. K., and R. A. BERNER, 1987. *The Global Water Cycle*. Prentice-Hall, Upper Saddle River, NJ, 397 pp.
- BROECKER, W. S., and T.-H. PENG, 1982. *Tracers in the Sea*. Eldigio Press, Palisades, NY, 690 pp.
- BULLEN, K. E., 1963. *An Introduction to the Theory of Seismology*, 3rd ed. Cambridge University Press, Cambridge, England, 381 pp.
- CLARKE, F. W., and H. S. WASHINGTON, 1924. *The Composition of the Earth's Crust*. U.S. Geol. Surv. Prof. Paper 127, 117 pp.
- DALY, R. A., 1914. *Igneous Rocks and Their Origin*. McGraw-Hill, New York, 563 pp.
- GOLDBERG, E. D. (Ed.), 1972. *The Sea*. Wiley, New York, 5 vols.
- GOLDSCHMIDT, V. M., 1954. *Geochemistry*. Oxford University Press, 730 pp.
- HART, S. R., and H. STAUDIGEL, 1982. The control of alkalis and uranium in seawater by ocean crust alteration. *Earth Planet. Sci. Lett.*, **58**:202-212.
- HENDERSON, P., 1982. *Inorganic Geochemistry*. Pergamon Press, Oxford, England, 353 pp.
- HERRMANN, A. G., 1970. Yttrium and the lanthanides. In K. H. Wedepohl (Ed.), *Handbook of Geochemistry*, vol. 2, part 5, ch. 39, sec. E, 57-71. Springer-Verlag, Berlin.
- HOLLAND, H. D., 1978. *The Chemistry of the Atmosphere and Oceans*. Wiley, New York, 351 pp.

- HUTCHISON, R., 1974. The formation of the Earth. *Nature*, **250**:556-568.
- KRAUSKOPF, K. B., 1979. *Introduction to Geochemistry*, 2nd ed. McGraw-Hill, New York, 617 pp.
- LI, Y.-H., 1982. A brief discussion on the mean oceanic residence time of elements. *Geochim. Cosmochim. Acta*, **46**:2671-2675.
- LISITSYN, A. P., et al., 1982. The relation between element influx from rivers and accumulation in ocean sediments. *Geochem. Int.*, **19**:102-110.
- MASON, B., 1966. *Principles of Geochemistry*, 3rd ed. Wiley, New York, 329 pp.
- MOORES, E. M., 1982. Origin and emplacement of ophiolites. *Rev. Geophys. Space Phys.*, **20**:735.
- PARKER, R. L., 1967. Composition of the Earth's crust. In M. Fleischer (Ed.), *Data of Geochemistry*. U.S. Geol. Surv. Prof. Paper 440D, 1-19.
- POLDERVAART, A., 1955. Chemistry of the earth's crust. In A. Poldervaart (Ed.), *Crust of the Earth—A Symposium*. Geol. Soc. Amer. Spec. Paper 62, 119-144.
- RILEY, J. P., and R. CHESTER, 1971. *Introduction to Marine Chemistry*. Academic Press, New York, 465 pp.
- RINGWOOD, A. E., 1966. The chemical composition and origin of the Earth. In P. M. Hurley (Ed.), *Advances in Earth Sciences*, 287-356. MIT Press, Cambridge, MA.
- RONOV, A. B., and A. A. YAROSHEVSKY, 1976. A new model for the chemical structure of the Earth's crust. *Geochem. Int.*, **13**(6):89-121.
- SEDERHOLM, J. J., 1925. The average composition of the earth's crust in Finland. *Comm. géol. Finlande Bull.*, **12**(70), 20 pp.
- TAYLOR, S. R., 1964. The abundance of chemical elements in the continental crust—a new table. *Geochim. Cosmochim. Acta*, **28**:1273-1285.
- TAYLOR, S. R., and S. M. MCLENNAN, 1985. *The Continental Crust: Its Composition and Evolution*. Blackwell Scientific Publ., Oxford, England, 312 pp.
- TUREKIAN, K. K., and K. H. WEDEPOHL, 1961. Distribution of the elements in some major units of the Earth's crust. *Geol. Soc. Amer. Bull.*, **72**:175-192.
- VINOGRADOV, A. P., 1962. Average contents of chemical elements in the principal types of igneous rocks of the Earth's crust. *Geochemistry*, **1962**(7):641-664.
- WEAST, R. C., M. J. ASTLE, and W. H. BEYER (Eds.), 1986. *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton, FL.
- WEDEPOHL, K. H., 1969. *Handbook of Geochemistry*, vol. 1. Springer-Verlag, Berlin, 442 pp.
- WHITFIELD, M., and D. R. TURNER, 1979. Water-rock partition coefficients and the composition of seawater and river water. *Nature*, **278**:132-137.

PRINCIPLES OF INORGANIC CHEMISTRY

An important task of geochemists is to understand the chemical compositions of minerals and rocks based on the physical and chemical properties of the elements and their atoms. The regular pattern of variation of the electronic structures of atoms determines the chemical properties of the elements and hence their positions in the periodic table. Consequently, our understanding of the distribution of chemical elements among the minerals and rocks of the Earth rests securely on the principles of physics and chemistry embodied in the periodic table.

The Electronic Structure of Atoms

We now end our tour of the stars and the solar system and turn to some basic principles of chemistry that will help us to understand the chemical processes taking place on the earthlike planets. The intellectual excitement generated by the exploration of the solar system cannot hide the fact that only on the Earth can we live without elaborate protection against the harsh environments of the other planets. This lesson of planetary exploration should increase our interest in our own planet and in the natural processes that take place on its surface and in its interior. We need to understand these processes well in order to assure adequate living conditions for future generations. For these reasons we now move to a description of atoms whose orbiting electrons resemble the orbiting planets and their satellites of the solar system.

5.1 The Atom of Thomson and Rutherford

Throughout the 19th century physicists accepted Sir Isaac Newton's opinion that atoms are "solid, massy, hard, impenetrable, moveable particles" (Jastrow, 1967, p. 9). However, in 1897 J. J. Thomson (1856–1940) discovered the electron and used it to develop a new model of the atom in which negatively charged electrons were thought to be embedded in a positively charged matrix like raisins in a plum pudding. In 1911 Niels Bohr (1885–1962) came to the Cavendish Laboratory at Cambridge as a postdoctoral fellow to work with Thomson on his electron theory. He argued

that the plum-pudding model of the atom could not be correct because it did not provide for the quantization of electromagnetic radiation that had been discovered by Max Planck (1858–1947) in Germany (Planck, 1900). However, Thomson was in no mood to argue with the 26-year-old Dane who had little knowledge of the English language at the time. Sir John, who was the director of the Cavendish Laboratory, had won the Nobel Prize in 1906, and had been knighted in 1908, was not interested in Bohr's ideas about how to improve his electron theory. Besides, he was then working on his "positive-ray apparatus," which would soon lead to the discovery of isotopes and the development of mass spectrometers (Holton, 1986).

Bohr therefore decided to leave Cambridge, and went to Manchester where Ernest Rutherford (1871–1937) was the Langworthy Professor of Physics. Perhaps as a test of Thomson's model of the atom, Rutherford had fired a beam of alpha particles at a piece of gold foil and had observed to his great surprise that the beam did not simply pass through the foil as expected. Instead, a significant number of alpha particles were scattered and some even seemed to bounce straight back as though they had struck a heavy object. He said later "It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you." (Jastrow, 1967, p. 9). After thinking about it, Rutherford decided that the massive objects had to be very small because they were struck only rarely by alpha particles and concluded that most

of the mass of the atom was concentrated in this small body, which he named the "nucleus."

Rutherford's model of the atom was inherently unstable because in classical physics an electron orbiting a positively charged nucleus loses energy by emitting an electromagnetic wave. As a result, the electron must speed up and the radius of its orbit must decrease until the electron crashes into the nucleus. Nevertheless, Bohr liked Rutherford's model because he had a hunch that he could improve it by extending the concept of quantization of electromagnetic energy to the mechanical energy of an electron orbiting the nucleus.

We all know that Bohr succeeded brilliantly, received the Nobel Prize in physics in 1922, and became one of the leaders in science in the 20th century. However, he had a hard time convincing even Rutherford that his model of the atom was right. When Bohr, who had briefly returned to Denmark, sent a manuscript copy of his paper, Rutherford agreed to submit it for publication but added, "I suppose you have no objection to my using my judgment to cut out any matter I may consider unnecessary in your paper?" (Holton, 1986, p. 240). Bohr did object and came back to Manchester from Copenhagen to discuss his paper with Rutherford point by point. In the end, Rutherford agreed to submit the entire manuscript, but grumbled that Bohr had been so obstinate.

When this paper and a second one were published (Bohr, 1913a, b), they were not well received. The prominent German physicist Otto Stern may have spoken for many of his colleagues when he reportedly said, "If this nonsense is correct, I will give up being a physicist." (Holton, 1986, p. 240). It was the end of an era. Physics was about to be shaken to its roots by quantum mechanics and the uncertainty principle.

5.2 Bohr's Theory of the Hydrogen Atom

The instability of an atom composed of one electron orbiting the nucleus can be demonstrated by means of Newtonian physics. We assume that the electron orbits the proton at a distance r and a

velocity v . The condition for stability of such an atom is that the force of electrostatic attraction must be equal to the centrifugal force:

$$\frac{e^2}{r^2} = \frac{mv^2}{r} \quad (5.1)$$

The energy of such an atom is the sum of the kinetic energy and the potential energy:

$$E = \frac{1}{2}mv^2 - \frac{e^2}{r} \quad (5.2)$$

The potential energy term has a negative sign because the electron is attracted toward the proton. From equation 5.1 we obtain:

$$m = \frac{e^2}{rv^2} \quad (5.3)$$

Substituting into equation 5.2 yields:

$$E = \frac{1}{2}\left(\frac{e^2}{r}\right) - \frac{e^2}{r} = -\frac{1}{2}\left(\frac{e^2}{r}\right) \quad (5.4)$$

We see from equation 5.4 that the energy of the atom is negative and that it is inversely related to the radius of the orbit. In the limit, the energy approaches minus infinity as the radius goes to zero.

The instability arises because the atom is an "energy well." Energy is liberated as the radius of the electron orbit decreases. Since there are no restrictions on the magnitude of the electronic radius in this model, atoms will tend to achieve a condition of minimum energy and maximum stability by reducing the radius to zero.

Bohr avoided this problem by specifying that the energy of the atom is not continuously variable but is, in fact, quantized so that the electron must be restricted to orbits having specific radii. In order to accomplish this, he postulated that the angular momentum of the electron is restricted to multiples of $h/2\pi$, where h is Planck's constant, which is equal to 6.62517×10^{-27} erg/sec (see also the inside back cover). Therefore, according to Bohr:

$$mvr = \frac{nh}{2\pi} \quad (5.5)$$

where $n = 1, 2, 3, \dots$, and is known as the first quantum number. However, the atom must still

satisfy the condition expressed by equation 5.1. Accordingly, the angular momentum of the electron must also be:

$$mvr = \frac{e^2}{v} \quad (5.6)$$

and a stable atom must satisfy both equations 5.5 and 5.6; thus:

$$\frac{e^2}{v} = \frac{nh}{2\pi} \quad (5.7)$$

The velocity of the electron is derivable from equation 5.5:

$$v = \frac{nh}{2\pi mr} \quad (5.8)$$

Substituting into equation (5.7) yields:

$$\frac{2\pi m r e^2}{nh} = \frac{nh}{2\pi} \quad (5.9)$$

which leads to:

$$r = \frac{n^2 h^2}{4\pi^2 m e^2} \quad (5.10)$$

Equation 5.10 indicates that the radius of the electron now depends on the square of the first quantum number multiplied by a constant a whose magnitude is:

$$a = \frac{h^2}{4\pi^2 m e^2} \quad (5.11)$$

The smallest radius permitted by Bohr's theory is obtained from equation 5.10 by setting $n = 1$, in which case:

$$r = a_0 = 0.529 \times 10^{-8} \text{ cm} \quad (5.12)$$

where a_0 is the so-called *Bohr radius*.

The energy of the atom can now be calculated by substituting equation 5.10 for the radius into equation 5.4 for the energy of the atom:

$$E = -\frac{1}{2}e^2 \left(\frac{4\pi^2 m e^2}{n^2 h^2} \right) = -\frac{2\pi^2 m e^4}{n^2 h^2} \quad (5.13)$$

We see that in Bohr's model the energy of the atom no longer depends on the radius of the electronic orbit but varies as the reciprocal of the

square of the first quantum number. Evidently, the quantum number plays a decisive role because it controls both the radius of the electronic orbit and the energy of the atom.

In Bohr's model of the atom the electron can occupy only certain orbits whose radii depend on the first quantum number. The energy of the atom varies in increments depending on which orbit the electron occupies. When the electron jumps from a higher orbit to a lower one, the energy of the atom decreases. The energy liberated in this way is radiated away as an electromagnetic wave. Bohr used an equation derived by Albert Einstein to represent this energy change.

If E_1 is the energy of the atom when the electron is in a particular orbit and E_2 is the energy when the electron is in a *smaller* orbit, then the change in the energy of the atom as the electron moves from orbit 1 to orbit 2 is:

$$E_1 - E_2 = \Delta E = h\nu \quad (5.14)$$

where ν is the frequency of the electromagnetic radiation and h is Planck's constant. The velocity of electromagnetic radiation c is related to its wavelength λ and the frequency ν by:

$$c = \lambda\nu \quad (5.15)$$

Therefore, the energy of the radiation emitted by an atom as a result of an electronic "transition" is:

$$\Delta E = \frac{hc}{\lambda} \quad (5.16)$$

In other words, the energy of the radiation is inversely proportional to its wavelength.

When Bohr developed this model of the atom between 1912 and 1913, it was already known that hydrogen atoms absorb and emit light at discrete wavelengths. These wavelengths had been expressed by the equation:

$$\frac{1}{\lambda} = R \left(\frac{1}{a_1^2} - \frac{1}{a_2^2} \right) \quad (5.17)$$

where a_1 and a_2 are whole numbers, $a_1 > a_2$, and R is the Rydberg constant, whose value was known to be $109,678.18 \text{ cm}^{-1}$. (Note that we use a in equation 5.17 instead of n in order to avoid confusion with the first quantum number.) By apply-

ing quantum mechanics to Rutherford's model of the hydrogen atom Bohr was able to calculate the wavelengths of light that hydrogen atoms can emit as a result of transitions among the orbits the electron can occupy. By combining equations 5.13, 5.14, and 5.16 we have:

$$\frac{2\pi^2me^4}{h^2}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = \frac{hc}{\lambda} \quad (5.18)$$

where n_1 and n_2 are the quantum numbers, and $n_2 > n_1$ as required by the Rydberg formula. It follows that:

$$\frac{1}{\lambda} = \frac{2\pi^2me^4}{h^3c}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \quad (5.19)$$

By comparing equations 5.19 (Bohr's model) and 5.17 (Rydberg formula) we see that:

$$R = \frac{2\pi^2me^4}{h^3c} \quad (5.20)$$

Bohr substituted appropriate values into equation 5.20 and calculated a value of $109,677.76 \text{ cm}^{-1}$ for the Rydberg constant. The result agreed very well with the observed value and thereby confirmed Bohr's model for the hydrogen atom. Niels Bohr was justifiably pleased with this result and subsequently devoted himself wholeheartedly to the study of quantum mechanics.

The Royal Danish Academy of Science, which receives a large portion of its funding from the Carlsberg Brewery, gave Bohr a grant of money to build an Institute for Theoretical Physics in Copenhagen. Bohr's institute became the center for research in quantum mechanics and nuclear physics. It was famous not only for its intellectual excitement but also for its relaxed atmosphere created by the "Professor" (Gamow, 1966).

5.3 Emission of X-rays

Bohr's model of the atom provided a direct explanation for the emission of x-rays, which had been discovered in 1895 by Wilhelm Konrad Röntgen (1845–1923). Although Bohr's model has been replaced by the wave mechanics of W. K. Heisenberg (1901–1976) and E. Schrödinger

(1887–1961), some aspects of it are still in use in the physics of x-rays.

In a commercial x-ray tube a stream of electrons is accelerated by a voltage difference in a vacuum before striking a target composed of a metal such as chromium, copper, molybdenum, or tungsten. The energetic electrons interact with the electrons of the target atoms and may knock them out of their orbits. X-rays are then generated when the resulting vacancies are filled by other electrons.

The wavelengths of these x-rays depend on the difference in the energies of the orbit in which a vacancy has been created and the orbit from which the replacing electron originated, as required by equation 5.16. These x-rays therefore have discrete wavelengths and give rise to a wavelength spectrum that is characteristic of the target element. The characteristic x-ray spectra were discovered in 1911 by Charles G. Barkla (1877–1944), who received the Nobel Prize for physics in 1917. The relationship between the characteristic x-ray spectrum and the atomic number of the target element was discovered in 1913 by H. G. J. Moseley (1877–1915).

In addition to the characteristic wavelength spectrum, a continuous x-ray spectrum is produced by electrons that pass through the target atoms without actually colliding with any of their electrons. Nevertheless, some energy is transferred in this type of interaction, and this energy is emitted as x-rays having continuously varying wavelengths.

The characteristic x-ray spectrum of the target atoms is divided into several series of wavelengths referred to by the letters K, L, M, etc. The "K x-rays" are emitted when a vacancy in the lowest energy level (K; $n = 1$) is filled. The electron filling the vacancy in the K-level may originate from the next higher level (L) or from others associated with electronic orbits having still larger radii. The L-series of characteristic x-rays is generated by transitions to the L-level ($n = 2$), and so on. The general scheme of identifying the characteristic x-rays is more complicated than that shown in Figure 5.1 because electrons in each of the K-, L-, and M-energy levels have slightly

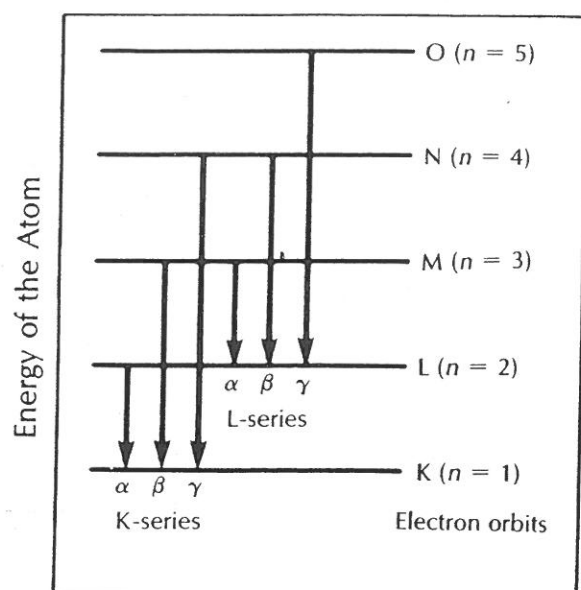


Figure 5.1 Schematic energy level diagram of atoms based on Bohr's model. X-rays of the K-series are generated by electronic transitions to the K-energy level ($n = 1$), whereas the L-series involves transitions to the L-level ($n = 2$). Greek letters are used to indicate the orbit from which the electrons originate. In reality the characteristic wavelength spectrum is more complicated than shown here because of small differences in the energies of the electrons that populate the M-, N-, and O-energy levels.

different energies. These differences are explainable in terms of wave mechanics and are not predicted in Bohr's model of the atom.

We see in Figure 5.1 that the K-series of characteristic x-rays is subdivided according to a simple scheme.

Electronic transition	Characteristic x-ray
L to K	K-alpha
M to K	K-beta
N to K	K-gamma
O to K	K-delta

The L-series is subdivided similarly, but the details in both series get more complicated

because of the "splitting" of the wavelengths caused by small energy differences of the electrons. In general, K-alpha x-rays are produced in greatest abundance because vacancies in the K-energy level are most often filled by electrons from the overlying L-level. Therefore, K-alpha x-rays are usually selected for analytical purposes both in x-ray-diffraction and in x-ray-fluorescence studies. The K-beta and K-gamma x-rays are more energetic, but their intensities are less than those of the K-alpha x-rays because the respective transitions occur less frequently.

X-ray diffraction and x-ray fluorescence have become indispensable tools in geochemical research. The former is based on the diffraction of x-rays by crystals (Klug and Alexander, 1954), whereas the latter arises from the emission of characteristic x-ray by atoms. X-ray fluorescence is now used to determine the chemical compositions of rocks including not only the major elements but also many trace elements (Norrish and Hutton, 1969).

5.4 Schrödinger's Model of the Atom

Bohr's model worked for the hydrogen atom and for ions having only one electron such as He^+ , Li^{2+} , and Be^{3+} . However, it did not work well for atoms having two or more electrons. Arnold Sommerfeld (1868–1951) made some improvements by introducing elliptical orbits like those of the planets in the solar system. In addition, he allowed the planes of the orbits to include all the free space around the nucleus, thereby making the atom look more like a sphere than a flat disk. These refinements of Bohr's model required the introduction of a second quantum number but still did not make it applicable to multielectron atoms.

The problem with Bohr's model is that it treats electrons as particles whose positions in space can be determined. The validity of this idea was questioned by Louis-Victor 7th Duke de Broglie

(1892–1987) in 1923 who demonstrated that particles such as electrons also have the properties of waves. The wavelength λ of particles of mass m and velocity v is:

$$\lambda = \frac{h}{mv} \quad (5.21)$$

where h is Planck's constant. For example, the wavelength of an electron having a kinetic energy of 10 electron volts is 0.12×10^{-8} cm, corresponding to fairly energetic x-rays (Moore, 1955, p. 271).

If electrons have wave properties, then it makes no sense to think of one as being in a particular place at a particular time. Werner Heisenberg expressed this condition in the form of the *uncertainty principle*, which implies that the motion of an electron around the nucleus of an atom cannot be described in terms of specific orbits regardless of whether they are circular or elliptical.

These strange ideas were incorporated into a new model of the atom proposed in 1926 by Werner Heisenberg and Erwin Schrödinger. Heisenberg's method was abstract and relied on matrix algebra, whereas Schrödinger (1926) used de Broglie waves to represent the distribution of electrons in three-dimensional space. Schrödinger's equation is generally stated in the form:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad (5.22)$$

where ψ is a "wave function," m is the mass of the electron, E is the total energy of the atom, and V is the potential energy (Fyfe, 1964).

The wave equation can be understood by comparing it to a violin string vibrating between two fixed points. Such a string can develop nodes whose number may be 0, 1, 2, etc. The number of nodes in the one-dimensional case is determined by the quantum number n . If $n = 1$, the number of nodes is zero; when $n = 2$ there is one node, and so on. In the three-dimensional electron wave, nodes may form along the three principal directions; therefore at least three quantum num-

bers are needed to describe the motions of an electron in the space around the nucleus of an atom. These quantum numbers are:

$$n = 1, 2, 3, \dots, \infty$$

(principal quantum numbers)

$$l = n - 1, n - 2, n - 3, \dots, 0$$

(azimuthal quantum number)

$$m = 0, \pm 1, \pm 2, \dots, \pm (l - 1), \pm l$$

(magnetic quantum number)

$$s = \pm \frac{1}{2} \quad (\text{spin quantum number})$$

The fourth quantum number, s , indicates the direction of spin of the electron, which controls the polarity of the magnetic moment exerted by the electron. Note that the electron is again regarded as a charged particle in space in this context.

Solutions to the wave equation are obtained for wave functions having certain types of symmetry in space. For example, the wave function can have spherical symmetry around the nucleus, or it may be symmetrical with respect to the x , y , z directions or the xy , xz , yz planes. In general, four different types of wave functions are possible, which are identified by the letters s , p , d , and f . These wave functions describe the motions of the electron to which they apply and are therefore called "orbitals" in order to distinguish them from the "orbits" of the Bohr–Sommerfeld model. The s -orbital has spherical symmetry about the nucleus. The p -type orbital is symmetrical about the x -, y -, and z -axes, and the d -orbitals are symmetrical about the xy , xz , and yz planes. These orbitals are pictured in Figure 5.2. The f -type orbitals cannot be pictured in three dimensions. In the case of the s -type wave function there is only one solution; but there are three p -orbitals corresponding to the principal axes, five d -orbitals, and seven f -orbitals.

The wave functions of the different types of orbitals convey the probability that the electron of the hydrogen atom will be found in a certain volume of space. Consequently, we can illustrate the distribution of the electron around the nucleus by plotting the function $4\pi r^2 \psi^2$ versus

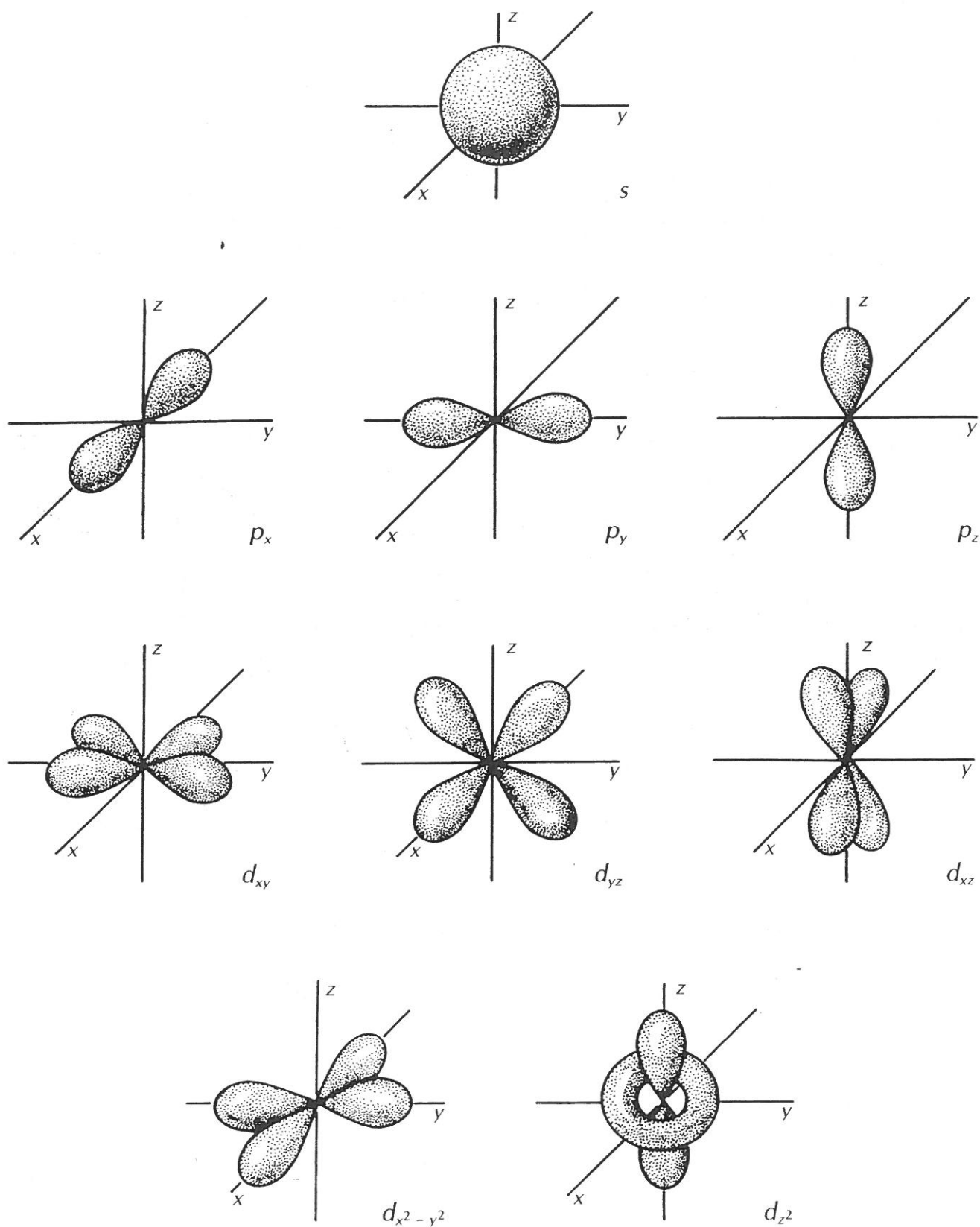


Figure 5.2 Electron clouds representing the s -, p -, and d -orbitals of the hydrogen atom according to the wave mechanical model of Schrödinger.

the distance r from the nucleus. Figure 5.3 is such a cross section of an s -orbital for the hydrogen atom. We see that the profile has a maximum at a distance $r = a_0$, the radius of the first electron orbit in Bohr's model. However, we also see that the electron can be found closer to or farther away from the nucleus some of the time. In other words, the electron actually occupies *all* of the space around the nucleus but can be found most often at a distance of a_0 from the nucleus. The same is true for all orbitals, and the orbital balloons shown in Figure 5.2 therefore have a "fuzzy" skin. The electrons occupying these orbitals do not spend all of their time on the skins of the balloons but move in and out in a random pattern predictable only in terms of probability. This aspect of quantum mechanics was very disturbing to Albert Einstein and even to Erwin Schrödinger. Einstein objected to the element of chance implied by the proba-

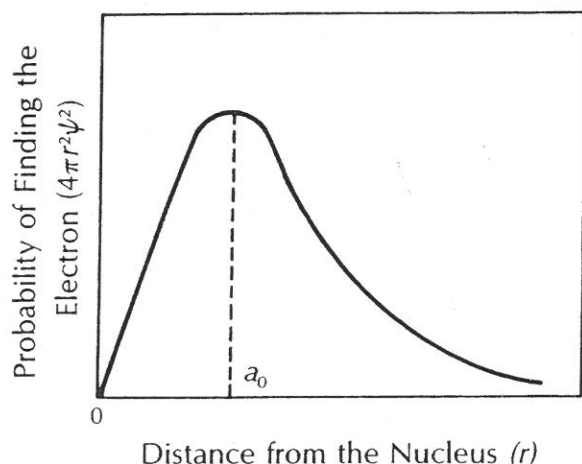


Figure 5.3 Variation of the radial distribution function ($4\pi r^2 \psi^2$) for the s -orbital with increasing distance from the nucleus (r). The radial distribution function is a measure of the probability of finding the electron at a certain distance from the nucleus. In the s -orbital this probability has a maximum at a distance $r = a_0$, where a_0 is the radius of the smallest orbit ($n = 1$) permitted by Bohr's model. We see that the electron in an s -orbital can also be found inside as well as outside that radius. The electron in effect occupies all of the space around the nucleus but can be found most often at the distance from the nucleus predicted by Bohr.

bilistic description of the electronic structure of atoms by saying "Der liebe Gott würfelt nicht!" (the good Lord does not throw dice).

5.5 The Aufbau Principle

We are now ready to begin the construction of atoms of increasing atomic number by adding electrons to the possible orbitals of the hydrogen atom. This procedure is known as the *Aufbau principle* by means of which the orbitals of the hydrogen atoms are used to make multielectron atoms. In doing so we assume that the number of protons in the nucleus increases in step with the electrons.

The energy of an atom having a certain number of electrons depends on the orbitals the electrons occupy. Therefore, the electrons occupy only those orbitals that *minimize* the resulting energy of the atom because the *lowest* energy state of an atom is also its *most stable* or "stationary" state. This requirement controls the *sequence* in which orbitals are filled. The sequence can be derived by calculating the energy of an atom for different electron configurations. However, for multielectron atoms these calculations become very difficult and must be supplemented by spectroscopic studies.

The four quantum numbers play an important role in this process because, according to Pauli's exclusion principle, no two electrons in one atom can have the same set of quantum numbers. This principle therefore limits the number of electrons that can enter a particular orbital. The relationship between the quantum numbers and the different orbitals is indicated in Table 5.1.

We see there that the quantum numbers allow only the s -orbital for $n = 1$; s -, and p -orbitals for $n = 2$; s -, p -, d -orbitals for $n = 3$; and s -, p -, d -, and f -orbitals when $n = 4$. The table also indicates that there are three different p -orbitals, five d -orbitals (the seven f -orbitals are not listed). Moreover, each individual orbital can accommodate two electrons provided their spin numbers are different. As a result, only two electrons can be accommodated in orbitals having

Table 5.1 Quantum Numbers and Possible Orbitals of the Hydrogen Atom

Quantum numbers				Type of orbital
n	l	m	s	
1	0	0	$+\frac{1}{2}, -\frac{1}{2}$	1s
2	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2s
2	1	0	$+\frac{1}{2}, -\frac{1}{2}$	2p
2	1	1	$+\frac{1}{2}, -\frac{1}{2}$	2p
2	1	-1	$+\frac{1}{2}, -\frac{1}{2}$	2p
3	0	0	$+\frac{1}{2}, -\frac{1}{2}$	3s
3	1	0	$+\frac{1}{2}, -\frac{1}{2}$	3p
3	1	1	$+\frac{1}{2}, -\frac{1}{2}$	3p
3	1	-1	$+\frac{1}{2}, -\frac{1}{2}$	3p
3	2	0	$+\frac{1}{2}, -\frac{1}{2}$	3d
3	2	1	$+\frac{1}{2}, -\frac{1}{2}$	3d
3	2	-1	$+\frac{1}{2}, -\frac{1}{2}$	3d
3	2	2	$+\frac{1}{2}, -\frac{1}{2}$	3d
3	2	-2	$+\frac{1}{2}, -\frac{1}{2}$	3d
etc.				

$n = 1$, eight electrons for $n = 2$, and 18 electrons for $n = 3$.

The sequence in which electronic orbitals are actually filled is:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s,
4d, 5p, 6s, 4f, 5d, 6p, 7s, 6d

The Aufbau principle, by means of which we can predict the electronic configuration of the elements in the periodic table, is governed by a set of rules we state here in plain language without regard to their historical origins.

1. The first electron enters the orbital having the lowest energy. Additional electrons enter orbitals that minimize the energy of the atom (see above).
2. Each orbital can accommodate two electrons provided their spins are opposite.
3. When electrons enter a particular set of orbitals, they distribute themselves such that each orbital at first acquires only one electron.

Subsequently, a second electron may enter an orbital that already contains an electron provided its spin is opposite (rule 2).

4. Atoms achieve a state of decreased energy and enhanced stability when the available orbitals are either completely filled, half-filled, or empty.

We are now ready to construct the atoms of the elements in order of increasing atomic number by specifying their electronic structures. We do this by stating the value of the first quantum number, the type of orbital, and the number of electrons in each of those orbitals. For example, $1s^2 2s^2 2p^3$ is the electronic structure of nitrogen (atomic number 7). It has two electrons in the 1s orbital, two in the 2s orbital, and three in the 2p orbitals. Evidently, each of the three *p*-orbitals contains one electron. We can anticipate from rule 4 that nitrogen atoms may attract three additional electrons to themselves in order to fill the *p*-orbitals. In addition, they may also empty the *p*-orbitals by giving up three electrons, or lose five electrons by emptying both the *p*- and *s*-orbitals having $n = 2$. Consequently, nitrogen is likely to have different *oxidation states* or *valences*: -3, 0, +3, and +5. Evidently, we are already able to make predictions about the chemical properties of nitrogen based entirely on its electronic structure and the principles of wave mechanics.

Table 5.2 lists the electronic "formulas" of the elements in order of increasing atomic number from 1 to 96. The electrons are inserted into the orbitals in the proper sequence. The highest positive oxidation state of each element can be anticipated by means of rule 4. We have no difficulty in assigning hydrogen an oxidation state or valence of +1, although -1 is also possible and occurs in hydrides such as LiH. In natural systems hydrogen has a valence of +1, or 0 when it occurs as the diatomic molecule H_2 .

Helium ($1s^2$) has filled the only orbital available to it, and therefore it neither accepts nor gives up additional electrons. Its valence is 0.

Lithium ($1s^2 2s^1$) begins a series of elements that fill orbitals having $n = 2$. The lone electron in

the $2s$ orbital of lithium exists outside the closed $1s^2$ orbital and is therefore readily lost. Hence lithium has a valence of +1.

Beryllium ($1s^2 2s^2$) has two electrons in the $2s$ orbital, but it gives them up easily, thereby acquiring a valence of +2.

Boron ($1s^2 2s^2 2p^1$) starts a sequence of six elements in which the $2p$ orbitals are filled. The positive valences of these elements follow logically: boron +3, carbon +4, nitrogen +5. The next element, oxygen ($1s^2 2s^2 2p^4$), should have a valence of +6; but its valence in nature actually is -2 because, after the p -orbitals are half-full (nitrogen), atoms of oxygen attract electrons to themselves in order to fill their orbitals. Even nitrogen can acquire three electrons and have a valence of -3 as, for example, in ammonia (NH_3). Fluorine ($1s^2 2s^2 2p^5$) has the strongest tendency of all the elements to attract electrons to itself and, consequently, has a valence of -1. Neon ($1s^2 2s^2 2p^6$) completes the sequence by filling the $2p$ orbital and thereby ends the series of elements that started with lithium. In Table 5.2 square brackets indicate that the noble gases have filled orbitals. Neon is an inert or "noble" chemical element that does not form bonds with other elements.

In the next sequence the s - and p -orbitals of the third shell are filled. The valences of these elements (sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, and argon) follow predictably from their electronic structures. Sodium has a $3s^1$ electron outside of a neon core and therefore has a valence of +1, just like lithium and hydrogen. Magnesium follows with +2, like beryllium before it, and so on. The electronic configuration of sulfur ($[\text{Ne}]3s^2 3p^4$) resembles that of oxygen, which has a valence of -2 because it strongly attracts electrons to itself. Sulfur atoms likewise attract two electrons to form S^{2-} , but they can also release their p -electrons and then assume a valence of +6, as in the sulfate ion (SO_4^{2-}). Chlorine strongly prefers the valence of -1 but takes a valence of +7 in the perchlorate (ClO_4^-) ion. Argon ($[\text{Ne}]3s^2 3p^6$) closes this sequence with a valence of 0.

The third energy shell includes d -type orbitals; however, potassium ($[\text{Ar}]4s^1$) puts the next electron into the $4s$ orbital rather than one of the $3d$ orbitals. Calcium ($[\text{Ar}]4s^2$) does likewise, so these elements have valences of +1 and +2, respectively. The d -orbitals are filled next, as we progress from scandium to zinc. In this sequence, chromium and copper are starred in Table 5.2 to draw attention to a significant anomaly in their electronic structures. Chromium should be $[\text{Ar}]3d^4 4s^2$ but is actually $[\text{Ar}]3d^5 4s^1$, and copper is $[\text{Ar}]3d^{10} 4s^1$. Both exemplify the benefit of half-filling or filling a set of electronic orbitals. Irregularity also occurs in the cases of iron, cobalt, and nickel because their valences do not follow the expected pattern. All three elements have valences of +2 and +3, even though we might have predicted +4 for cobalt and +5 for nickel.

Next, we have another sequence of six elements, starting with gallium and ending with krypton, in which the $4p$ orbitals are filled. These elements are similar to the aluminum-argon series in which $3p$ orbitals are filled.

Table 5.2 continues with another 18 elements: rubidium and strontium ($5s$), yttrium to cadmium ($4d$), and indium to xenon ($5p$). After that come elements with electrons in $6s$, $4f$, $5d$, and $6p$ orbitals ending with radon (atomic number 86). The sequence continues with $7s$, $6d$, and $5f$ through the transuranium series. In general, the chemical properties of elements having partially filled d - and f -orbitals do not vary as much as those in which s - and p -orbitals are being filled.

5.6 Summary

Our concept of the internal structure of the atom has undergone many changes since J. J. Thomson formulated the "plum-pudding model." Some of the important milestones in this evolution are the scattering of alpha particles, discovered by E. Rutherford; the quantization of the energy of the hydrogen atom by N. Bohr; and the demonstration by L. V. de Broglie that small particles have wave properties. Ultimately W. K. Heisenberg and E. Schrödinger described the energy states of

Table 5.2 Electronic Structure and Valences of the Elements

Z^a	Element	Electronic structure	Valences
1	Hydrogen	$1s^1$	+1, -1
2	Helium	$1s^2$	0
3	Lithium	$1s^2 2s^1$	+1
4	Beryllium	$1s^2 2s^2$	+2
5	Boron	$1s^2 2s^2 2p^1$	+3
6	Carbon	$1s^2 2s^2 2p^2$	+4, +2, -4
7	Nitrogen	$1s^2 2s^2 2p^3$	+5, +4, +3, +2, -3
8	Oxygen	$1s^2 2s^2 2p^4$	+6, -2
9	Fluorine	$1s^2 2s^2 2p^5$	+7, -1
10	Neon	$1s^2 2s^2 2p^6$	0
11	Sodium	$[\text{Ne}]3s^1$	+1
12	Magnesium	$[\text{Ne}]3s^2$	+2
13	Aluminum	$[\text{Ne}]3s^2 3p^1$	+3
14	Silicon	$[\text{Ne}]3s^2 3p^2$	+4, -1
15	Phosphorus	$[\text{Ne}]3s^2 3p^3$	+5, +4, +3, -3
16	Sulfur	$[\text{Ne}]3s^2 3p^4$	+6, +4, +2, -2
17	Chlorine	$[\text{Ne}]3s^2 3p^5$	+7, +5, +3, +1, -1
18	Argon	$[\text{Ne}]3s^2 3p^6$	0
19	Potassium	$[\text{Ar}]4s^1$	+1
20	Calcium	$[\text{Ar}]4s^2$	+2
21	Scandium	$[\text{Ar}]3d^1 4s^2$	+3
22	Titanium	$[\text{Ar}]3d^2 4s^2$	+4, +3
23	Vanadium	$[\text{Ar}]3d^3 4s^2$	+5, +4, +3, +2
24*	Chromium	$[\text{Ar}]3d^5 4s^1$	+6, +3, +2
25	Manganese	$[\text{Ar}]3d^5 4s^2$	+7, +6, +4, +3, +2
26	Iron	$[\text{Ar}]3d^6 4s^2$	+3, +2
27	Cobalt	$[\text{Ar}]3d^7 4s^2$	+3, +2
28	Nickel	$[\text{Ar}]3d^8 4s^2$	+3, +2
29*	Copper	$[\text{Ar}]3d^{10} 4s^1$	+2, +1
30	Zinc	$[\text{Ar}]3d^{10} 4s^2$	+2
31	Gallium	$[\text{Ar}]3d^{10} 4s^2 4p^1$	+3, +1
32	Germanium	$[\text{Ar}]3d^{10} 4s^2 4p^2$	+4, +2
33	Arsenic	$[\text{Ar}]3d^{10} 4s^2 4p^3$	+5, +3, -3
34	Selenium	$[\text{Ar}]3d^{10} 4s^2 4p^4$	+6, +4, -2
35	Bromine	$[\text{Ar}]3d^{10} 4s^2 4p^5$	+7, +5, +1, -1
36	Krypton	$[\text{Ar}]3d^{10} 4s^2 4p^6$	0
37	Rubidium	$[\text{Kr}]5s^1$	+1
38	Strontium	$[\text{Kr}]5s^2$	+2
39	Yttrium	$[\text{Kr}]4d^1 5s^2$	+3
40	Zirconium	$[\text{Kr}]4d^2 5s^2$	+4
41	Niobium	$[\text{Kr}]4d^3 5s^2$	+5, +3
42*	Molybdenum	$[\text{Kr}]4d^5 5s^1$	+6, +5, +4, +3, +2
43	Technetium	$[\text{Kr}]4d^5 5s^2$	+7
44	Ruthenium	$[\text{Kr}]4d^6 5s^2$	+8, +6, +4, +3, +2
45	Rhodium	$[\text{Kr}]4d^7 5s^2$	+4, +3, +2
46	Palladium	$[\text{Kr}]4d^8 5s^2$	+4, +2
47*	Silver	$[\text{Kr}]4d^{10} 5s^1$	+1
48	Cadmium	$[\text{Kr}]4d^{10} 5s^2$	+2
49	Indium	$[\text{Kr}]4d^{10} 5s^2 5p^1$	+3, +1

Table 5.2 (continued)

Z^a	Element	Electronic structure	Valences
50	Tin	$[\text{Kr}]4d^{10}5s^25p^2$	+4, +2
51	Antimony	$[\text{Kr}]4d^{10}5s^25p^3$	+5, +3, -3
52	Tellurium	$[\text{Kr}]4d^{10}5s^25p^4$	+6, +4, -2
53	Iodine	$[\text{Kr}]4d^{10}5s^25p^5$	+7, +5, +1, -1
54	Xenon	$[\text{Kr}]4d^{10}5s^25p^6$	0
55	Cesium	$[\text{Xe}]6s^1$	+1
56	Barium	$[\text{Xe}]6s^2$	+2
57	Lanthanum	$[\text{Xe}]5d^16s^2$	+3
58*	Cerium	$[\text{Xe}]4f^25d^06s^2$	+3, +4
59	Praseodymium	$[\text{Xe}]4f^35d^06s^2$	+3, +4
60	Neodymium	$[\text{Xe}]4f^45d^06s^2$	+3
61	Promethium	$[\text{Xe}]4f^55d^06s^2$	+3
62	Samarium	$[\text{Xe}]4f^65d^06s^2$	+3, +2
63	Europium	$[\text{Xe}]4f^75d^06s^2$	+3, +2
64*	Gadolinium	$[\text{Xe}]4f^75d^16s^2$	+3
65	Terbium	$[\text{Xe}]4f^95d^06s^2$	+3, +4
66	Dysprosium	$[\text{Xe}]4f^{10}5d^06s^2$	+3
67	Holmium	$[\text{Xe}]4f^{11}5d^06s^2$	+3
68	Erbium	$[\text{Xe}]4f^{12}5d^06s^2$	+3
69	Thullium	$[\text{Xe}]4f^{13}5d^06s^2$	+3, +2
70	Ytterbium	$[\text{Xe}]4f^{14}5d^06s^2$	+3, +2
71	Lutetium	$[\text{Xe}]4f^{14}5d^16s^2$	+3
72	Hafnium	$[\text{Xe}]4f^{14}5d^26s^2$	+4
73	Tantalum	$[\text{Xe}]4f^{14}5d^36s^2$	+5
74	Tungsten	$[\text{Xe}]4f^{14}5d^46s^2$	+6, +5, +4, +3, +2
75	Rhenium	$[\text{Xe}]4f^{14}5d^56s^2$	+7, +6, +4, +2, -1
76	Osmium	$[\text{Xe}]4f^{14}5d^66s^2$	+8, +6, +4, +3, +2
77	Iridium	$[\text{Xe}]4f^{14}5d^76s^2$	+6, +4, +3, +2
78*	Platinum	$[\text{Xe}]4f^{14}5d^96s^1$	+4, +2
79	Gold	$[\text{Xe}]4f^{14}5d^{10}6s^1$	+3, +1
80	Mercury	$[\text{Xe}]4f^{14}5d^{10}6s^2$	+2, +1
81	Thallium	$[\text{Xe}]4f^{14}5d^{10}6s^16p^1$	+3, +1
82	Lead	$[\text{Xe}]4f^{14}5d^{10}6s^26p^2$	+4, +2
83	Bismuth	$[\text{Xe}]4f^{14}5d^{10}6s^26p^3$	+5, +3
84	Polonium	$[\text{Xe}]4f^{14}5d^{10}6s^26p^4$	+4, +2
85	Astatine	$[\text{Xe}]4f^{14}5d^{10}6s^26p^5$	+7, +5, +3, +1, -1
86	Radon	$[\text{Xe}]4f^{14}5d^{10}6s^26p^6$	0
87	Francium	$[\text{Rn}]7s^1$	+1
88	Radium	$[\text{Rn}]7s^2$	+2
89	Actinium	$[\text{Rn}]6d^17s^2$	+3
90	Thorium	$[\text{Rn}]5f^06d^27s^2$	+4
91*	Protactinium	$[\text{Rn}]5f^26d^17s^2$	+5, +4
92	Uranium	$[\text{Rn}]5f^36d^17s^2$	+6, +5, +4, +3
93	Neptunium	$[\text{Rn}]5f^46d^17s^2$	+6, +5, +4, +3
94	Plutonium	$[\text{Rn}]5f^66d^07s^2$	+6, +5, +4, +3
95	Americium	$[\text{Rn}]5f^76d^07s^2$	+6, +5, +4, +3
96	Curium	$[\text{Rn}]5f^76d^17s^2$	+3

^aThe electron configuration of starred elements is irregular.

atoms in terms of electron orbitals based on the wave-mechanical treatment of the motions of electrons in the space around the nucleus. As a result, we can only describe the motion of an electron in terms of the probability of finding it at a particular point in space. Bohr's original model of the atom has been replaced by the wave-mechanical treatment except in the explanation for the generation of the characteristic x-ray spectra of the elements.

The electronic structure of the elements can be deduced from the possible orbitals of the hydrogen atom by means of the Aufbau principle together with a set of rules that tell us, in effect, how electrons distribute themselves in the available orbitals. We find that atoms change the num-

ber of electrons in such a way that partially filled orbitals are emptied completely, filled completely, or are occupied by only one electron per orbital in a set. This property of atoms can be used to explain the valences of the elements and hence their chemical properties.

We conclude that the chemical and physical properties of the elements depend on the number of protons in the nuclei of their atoms (atomic number) and on the distribution of the electrons around the available orbitals. Knowledge of the electronic structure of the elements therefore enhances our understanding of their chemical properties and provides a rational explanation for the construction of the periodic table.

Problems

1. Familiarize yourself with the names, chemical symbols, atomic numbers, and electronic structures of the first 36 elements.

2. How many electrons can be accommodated in orbitals having the quantum number $n = 4$? (Answer: 32)

3. Write a complete set of quantum numbers for $n = 4$.

4. Using the electronic formulas in Table 5.2, explain the valences of the following elements: Co, S, Br, V, and Cu.

5. What do the elements of each group have in common

- (a) B, Al, Ga, and In
- (b) Be, Mg, Ca, Sr, Ba, and Ra
- (c) N, P, As, Sb, and Bi
- (d) K^+ , Ca^{2+} , Sc^{3+} , Ti^{4+} , V^{5+} , Cr^{6+}

6. Without consulting Table 5.2, write the electron formula for a neutral atom having 14 electrons and predict its highest positive valence.

7. Table 5.2 suggests that the valences of the elements vary systematically with increasing atomic number. Determine how many sequences there are that end with a valence of zero.

8. Elements having similar chemical properties tend to be associated in nature. For the following pairs of elements indicate whether or not you expect them to be associated with each other. Base your answer on the electronic structures of these elements.

- (a) K and Rb
- (b) Al and Ge
- (c) Sc and Cu
- (d) S and Se
- (e) Li and Mg

References

- BOHR, N., 1913a. Binding of electrons by positive nuclei. *Phil. Mag. J. Sci., Ser. 6*, **26**(151):1-25.
- BOHR, N., 1913b. Systems containing only a single nucleus. *Phil. Mag. J. Sci., Ser. 6*, **26**(153):476-507.

- FYFE, W. S., 1964. *Geochemistry of Solids*. McGraw-Hill, New York, 199 pp.
- GAMOW, G., 1966. *Thirty Years That Shook Physics*. Doubleday, Garden City, NY, 224 pp.

- HOLTON, G., 1986. Niels Bohr and the integrity of science. *Amer. Scientist*, **74**:237-243.
- JASTROW, R., 1967. *Red Giants and White Dwarfs*. Harper & Row, New York, 176 pp.
- KLUG, H. P., and L. E. ALEXANDER, 1954. *X-ray Diffraction Procedures*. Wiley, New York, 716 pp.
- MOORE, W. J., 1955. *Physical Chemistry*, 2nd ed. Prentice-Hall, Upper Saddle River, NJ, 633 pp.
- NORRISH, K., and J. T. HUTTON, 1969. An accurate x-ray spectrographic method for the analysis of a wide range of geological samples. *Geochim. Cosmochim. Acta*, **33**:431-453.
- PLANCK, M., 1900. Zur Theorie des Gesetzes der Energieverteilung im Normalspectrum. *Verh. Deutschen Phys. Gesellschaft*, **2**(170):237-245.
- SCHRÖDINGER, E., 1926. Quantisierung als Eigenwertproblem, Part 1. *Ann. Phys.*, **79**(4):361-376; Part 2, **79**(6):489-527.

The Periodic Table and Atomic Weights

In the early part of the 19th century chemists were almost overwhelmed by the discovery of new elements. By 1830 the number of elements had increased to 55, and there was no way of knowing how many more remained to be discovered. This uncomfortable situation motivated efforts to organize the elements in some systematic ways that might bring order to this increasingly chaotic state of affairs.

6.1 Mendeleev's Periodic Table

Although many chemists contributed to the effort to organize the elements, Dmitri Ivanovich Mendeleev (1834–1907) deserves to be recognized as the inventor of the periodic table (Asimov, 1965; van Sprosen, 1969).

Mendeleev was a graduate student in Germany when Friedrich August Kekulé von Stradonitz (known as Kekulé) organized a meeting of the leading chemists of Europe in 1860 in Karlsruhe. The purpose of this "First International Chemical Congress" was to debate the merits of the structural formulas of organic compounds Kekulé had proposed in 1858. These formulas were based on the idea that carbon has a valence of 4 and bonds with hydrogen, and even with itself, to form increasingly complex molecular chains. During the Congress in Karlsruhe the Italian chemist Stanislao Cannizzaro urged the delegates to recognize the importance of the atomic weights of the elements and to distinguish them from the equivalent weights and the molecular weights

based on an hypothesis his colleague Amadeo Avogadro had advanced in 1811.

When Mendeleev returned to Russia he used both the valences and the atomic weights to organize the elements into periods. In 1869 he published a table in the *Journal of the Russian Chemical Society* in which he identified several periods within which the valences rose and fell in regular patterns. In the following year (1870), the German chemist Julius Lothar Meyer published a graph of atomic volumes plotted versus atomic weights that also revealed the periodicity of these properties. However, Mendeleev (1871) boldly reordered some elements in his table on the basis of their valences and left gaps where, he claimed, elements existed that had not yet been discovered. For example, he predicted the existence of an element similar to silicon and specified many of its physical and chemical properties by comparison with those of its neighbors in his table. His predictions were confirmed when C. A. Winkler discovered germanium in 1886 during the analysis of the rare mineral argyrodite (Ag_8GeS_6) (Weeks, 1956).

6.2 The Modern Periodic Table

The periodic table has assumed many forms since it was first presented by Mendeleev. Mazurs (1974) described over 700 different graphic representations. Today we use the so-called long form depicted in Figure 6.1.

The elements are arranged into horizontal rows called *periods* and vertical columns called

[illegible]

Figure 6.1 The periodic table of the elements. The numbering of the groups has been changed to run consecutively from 1 to 18 across the table. The old method is used here to emphasize the relationship between the electronic structures and highest positive valences of atoms.

groups. The periods are numbered in accordance with the first quantum number of the orbitals that are being filled with increasing atomic number. For example, the elements of the first period contain electrons in the $1s$ orbital, the elements of the second period have electrons in the $2s$ and $2p$ orbitals, those in third period are filling $3s$ and $3p$ orbitals, and in the fourth period electrons enter $4s$ and $4p$ orbitals. However, the fourth period contains an additional group of 10 elements in which the $3d$ orbitals are filling up. Similarly, the fifth and sixth periods each contain elements in which d -orbitals are being filled. These elements together form the so-called d -block in the periodic table. The sixth period contains 14 extra elements known as the *rare earths* with electrons in $4f$ orbitals. The rare earths are pulled out of the table and placed separately below it together with the *actinide elements* in which $5f$ orbitals are being filled and which include the *transuranium* or "super-heavy" elements. We see, therefore, that the number of the elements in each period is a direct consequence of the progressive filling of electronic orbitals. These relationships are evident in Table 6.1.

The numbering of the vertical columns or groups has been confusing to say the least. They used to be numbered from left to right in accordance with the highest positive valence of the ele-

ments in that group. In this version of the periodic table the elements in the s - and p -blocks formed the "A groups," and the elements in the d -block composed the "B groups." However, the identification of A and B groups has not been consistent. The valences of the elements in the A groups, as used in Figure 6.1, can be deduced directly from the electronic configurations of the atoms. For example, group IA consists of H, Li, Na, K, Rb, Cs, and Fr, each of which has one electron in an s -orbital outside of a noble gas core and thus a valence of +1. Excluding hydrogen, the elements in group IA are known as the *alkali metals*. The elements in group IIA, called the *alkaline earths*, include Be, Mg, Ca, Sr, Ba, and Ra. These elements have two electrons in an s -orbital outside a noble gas core and therefore have valences of +2.

The numbering of the A groups as defined above continues with the elements of the p -block on the right side of the periodic table. Once again the numbering corresponds to the highest positive valence consistent with the electronic configuration. Thus the elements in group 7A can have valences of +7 because they all have five electrons in p -orbitals and two electrons in s -orbitals. The elements in this group are called the *halogens* and include F, Cl, Br, I, and At. In nature the atoms of these elements attract an electron and actually form ions with a charge of -1 . Nevertheless, they have electronic structures that make a valence of +7 at least technically possible. The last group of elements are the *noble gases* He, Ne, Ar, Kr, Xe, and Rn, all of which have filled orbitals. Consequently, they neither gain nor lose electrons under natural conditions and therefore have a valence of 0. In spite of that fact, this group used to be given the number 8, although 0 is more appropriate.

Partly because of these kinds of inconsistencies, chemists have decided to number the groups consecutively from left to right. In this new scheme the alkali metals are still in group 1 but the noble gases are now in group 18 (Figure 6.1). Nevertheless, we will continue the old numbering system outlined above because it emphasizes the

Table 6.1 Relationship Between Periods and Electron Orbitals of Atoms of the Elements

Period	Orbitals being filled	Number of elements
1	$1s$	2
2	$2s, 2p$	8
3	$3s, 3p$	8
4	$4s, 3d, 4p$	18
5	$5s, 4d, 5p$	18
6	$6s, 4f, 5d, 6p$	32
7	$7s, 5f, 6d, 7p$	32 ^a

^aOnly 17 are known.

close relationship between the valence and the electronic structure of the elements.

The elements with incompletely filled d -orbitals are referred to as the *transition metals*. The groups in this block of elements are numbered in accordance with the valences of the elements just like the A groups. Therefore, group IB consists of the precious metals Cu, Ag, and Au, which have electron configurations of $d^{10}s^1$ and therefore can have a valence of +1. However, copper can also be +2, and gold can be +3. The numbering of the B groups continues with IIB composed of Zn, Cd, and Hg with $d^{10}s^2$ electron configurations that form +2 ions. Next, we move to the left to IIIB (Sc, Y, and La, d^1s^2 , valence +3) and progress from there to group VIIB (Mn, Tc, and Re, d^5s^2 , valence +7). However, the next three groups are anomalous. The iron group (Fe, Ru, and Os) should have a valence of +8 in accordance with their electronic structure (d^6s^2), but iron actually has valences of +2 and +3. Cobalt and nickel also have valences of +2 and +3. Therefore, these three groups are lumped together as group VIIIB. This is not a very elegant solution, but it has tradition on its side. The *congeners* of Fe, Co, and Ni form the *platinum group elements* (PGE) consisting of Ru, Os, Rh, Ir, Pd, and Pt. These elements can occur in the native state and, in addition, have valences of +2, +3, +4, +6, and even +8 in the case of Ru and Os.

The periodic table is founded on the recurrence of similar physical and chemical properties of the elements with increasing atomic number. This statement is known as the *periodic law* of the elements. In addition, elements in *groups* have the same valences because they have similar electronic structures. As a result, their physical and chemical properties tend to be similar.

In geochemistry this means that the elements of a group tend to occur together and display *geochemical coherence*. For example, the alkali metals, the alkaline earths, the halogens, the noble gases, and the precious metals display well-developed geochemical coherence in their distribution in nature.

6.3 Basic Principles of Atomic Physics

We know that atoms have nuclei composed of protons and neutrons. The number of protons in the nucleus determines the positive charge and therefore the number of extranuclear electrons required to form a neutral atom. The number of electrons and their distribution in the available orbitals give atoms their characteristic chemical properties. Therefore, the atomic number (Z) indirectly determines the chemical properties of an atom. Since all atoms of a chemical element must have the same (or nearly the same) chemical properties, it follows that all atoms of a given element must have the same atomic number.

The number (N) of neutrons in the nuclei of atoms affects atomic masses but has no direct bearing on chemical properties. Therefore, atoms of the same chemical element may contain different numbers of neutrons in their nuclei. Atoms that have the same atomic number but different neutron numbers are called *isotopes*. The word means "same place" and indicates that the isotopes of an element all occupy the same place in the periodic table because they have the same (or very similar) chemical properties.

The internal composition of the nuclei of isotopes is indicated by the shorthand notation used to identify them. This notation consists of the chemical symbol of the element, preceded by the atomic number (Z) written as a subscript, and the mass number (A) written as a superscript, where:

$$A = Z + N \quad (6.1)$$

Therefore, the notation $^{12}_6\text{C}$ indicates that the atom or *nuclide* is an isotope of carbon, that its nucleus contains 6 protons, and that the sum of protons and neutrons is 12. From equation 6.1 we find that the nucleus also contains 6 neutrons.

Most chemical elements have two or more stable isotopes. However, some elements, including Be, F, Na, Al, P, Mn, Co, and As have only one stable

isotope. Several other elements, including K, Rb, Sm, Lu, Re, Th, and U, have long-lived radioactive isotopes that decay so slowly that they still occur in the solar system even though they formed more than 6×10^9 years ago by nucleosynthesis reactions in ancestral stars. In addition, more than 2000 short-lived radioactive isotopes are known that do not occur in nature because they have decayed since the time of nucleosynthesis.

A fairly large group of short-lived radioactive isotopes *does* occur in nature because these isotopes are continuously produced either by the decay of long-lived parents (U and Th) or by nuclear reactions involving cosmic rays. The unstable daughters of uranium and thorium are polonium, astatine, radon, francium, radium, actinium, and protactinium. Another large number of radioactive isotopes is produced by nuclear reactions in the atmosphere: tritium, ^3_1H , $^{10}_4\text{Be}$, $^{14}_6\text{C}$, $^{36}_{17}\text{Cl}$, and many others.

The abundances of the naturally occurring isotopes (stable or long-lived radioactive) are determined with mass spectrometers and are expressed in percent by *number*. For example, boron has two stable isotopes whose abundances are $^{10}_5\text{B} = 19.8\%$ and $^{11}_5\text{B} = 80.2\%$. This means that out of 1000 boron atoms 198 are the isotope $^{10}_5\text{B}$ and 802 are $^{11}_5\text{B}$. Actually, it turns out that the isotopic compositions of boron and of other elements of low atomic number (H, C, N, O, and S) may be changed by *isotope fractionation* because mass differences among the isotopes of an element affect the kinetics of chemical reactions and the strengths of chemical bonds. These effects are part of the subject of isotope geoscience presented in detail in a textbook by Faure (1986) and will be discussed in Chapter 18 of this book.

6.4 Atomic Weights

The concept of the *atomic weight* is fundamental to all forms of chemistry but is not always clearly understood. One reason for the uncertainty is that the scale by means of which atomic weights are

expressed has changed over the years. Originally, chemists used oxygen as the standard and gave it an atomic weight of 16.0000. However, after the discovery of isotopes, physicists adopted a different scale based on $^{16}_8\text{O} = 16.0000$. All of the resulting confusion has now been eliminated by the adoption of $^{12}_6\text{C}$ as the standard. Therefore, the masses of atoms are now expressed in the atomic mass unit (amu), defined as 1/12 of the mass of $^{12}_6\text{C}$, which is the most abundant stable isotope of carbon. The masses of the naturally occurring isotopes have also been determined by mass spectrometry, and the results are tabulated in standard reference books such as the *CRC Handbook of Chemistry and Physics* (Weast et al., 1986).

We are now ready to define the atomic weight of an element.

The atomic weight of an element is the sum of the masses of its naturally occurring isotopes weighted in accordance with their abundances.

An example will clarify what this means. Silicon has three naturally occurring stable isotopes whose abundances and masses are

Isotope	Abundance, %	Mass, amu
$^{28}_{14}\text{Si}$	92.23	27.976 927
$^{29}_{14}\text{Si}$	4.67	28.976 495
$^{30}_{14}\text{Si}$	3.10	29.973 770

The atomic weight of silicon is found by multiplying the masses of the isotopes by their abundances expressed as decimal fractions and adding the resulting products:

$$^{28}_{14}\text{Si}: 0.9223 \times 27.976\,927 = 25.803\,12$$

$$^{29}_{14}\text{Si}: 0.0467 \times 28.976\,495 = 1.353\,20$$

$$^{30}_{14}\text{Si}: 0.0310 \times 29.973\,770 = 0.929\,18$$

$$\text{Sum} = 28.085\,50$$

Therefore, the atomic weight of silicon, rounded to five significant figures, is 28.086. Chemists regard the atomic weights of the elements as dimension-

less numbers because they are expressed relative to the mass of $^{12}_6\text{C}$ (Greenwood and Earnshaw, 1984).

The importance of the atomic weights of the elements arises from their use in the definition of the gram-atomic weight.

The *gram-atomic weight* of an element is equal to the atomic weight in grams.

Similarly, the gram-molecular weight or the gram-formula weight of a compound is defined as

The *gram-molecular weight* (or the *gram-formula weight*) of a compound is the molecular weight (or formula weight) in grams.

Both the gram-atomic weight and gram-molecular weight are referred to as the *mole* (mol). This is the basic unit of mass of elements and compounds in chemistry.

The reason why the mole is so important in chemistry is that one mole of an element or a compound always contains a fixed number of atoms or molecules. That number is:

$$N_A = 6.022\,045 \times 10^{23} \text{ atoms or molecules per mole}$$

which is known as *Avogadro's number*. It is a consequence of the hypothesis proposed by Amadeo Avogadro in 1811 that equal volumes of gases at the same pressure and temperature contain equal numbers of atoms or molecules. Therefore, the concept of the mole together with Avogadro's number enables us to convert an amount of an element or compound from grams to the corresponding number of atoms or molecules. In addition, we can now appreciate the formal definition of the mole stated on the inside back cover of this book.

The *mole* is the amount of a system that contains as many elementary entities as there are atoms in 0.012 kg of carbon-12.

In other words, 6.022×10^{23} atoms, molecules, ions, electrons, or other specified particles make up one mole.

The relationship between moles and the corresponding number of atoms and molecules enables us to represent chemical reactions by means of equations. For example, the equation:



indicates that two molecules of hydrogen (H_2) must combine with one molecule of oxygen (O_2) in order to form two molecules of water (H_2O). If we mix 2 g of H_2 with 1 g of O_2 we would *not* achieve the desired proportions of molecules. However, when the amounts of H_2 and O_2 are expressed in terms of moles, then the H_2 and O_2 molecules will be present with the necessary 2:1 ratio required for the reaction.

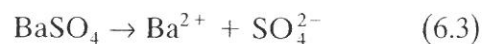
The atomic weights of the elements listed in Table 6.2 enable us to calculate molecular weights of compounds based on their chemical formulas and to convert amounts of such compounds from grams to the corresponding number of moles. For example, the molecular weight of BaSO_4 (barite) is calculated from the atomic weights of the elements:

Ba:	137.33
S:	32.06
O:	15.9994

The molecular weight of barite is 233.366, and one mole of barite weighs 233.366 g. The solubility of barite in cold water is 2.22×10^{-4} g/100 mL (Weast et al., 1986). Therefore, one liter of a saturated solution contains 2.22×10^{-3} g of barite, which corresponds to:

$$\frac{2.22 \times 10^{-3}}{233.366} = 9.513 \times 10^{-6} \text{ mol}$$

When barite dissolves in water, it dissociates into ions:



The equation indicates that each mole of barite that dissolves produces one mole of Ba^{2+} and one mole of SO_4^{2-} . Since 9.512×10^{-6} mol of barite dissolves in 1 L of a saturated solution, the concentration of

Table 6.2 Atomic Weights of the Elements Relative to $^{12}_6\text{C}$

<i>Z</i>	<i>Element</i>	<i>Atomic Weight</i>	<i>Z</i>	<i>Element</i>	<i>Atomic Weight</i>
1	H	1.00794	48	Cd	112.41
2	He	4.00260	49	In	114.82
3	Li	6.941	50	Sn	118.71
4	Be	9.01218	51	Sb	121.75
5	B	10.81	52	Te	127.60
6	C	12.011	53	I	126.905
7	N	14.0067	54	Xe	131.29
8	O	15.9994	55	Cs	132.905
9	F	18.9984	56	Ba	137.33
10	Ne	20.179	57	La	138.906
11	Na	22.9898	58	Ce	140.12
12	Mg	24.305	59	Pr	140.908
13	Al	26.9815	60	Nd	144.24
14	Si	28.0855	61	Pm	(145) ^a
15	P	30.9738	62	Sm	150.36
16	S	32.06	63	Eu	151.96
17	Cl	35.453	64	Gd	157.25
18	Ar	39.948	65	Tb	158.925
19	K	39.0983	66	Dy	162.50
20	Ca	40.08	67	Ho	164.930
21	Sc	44.9559	68	Er	167.26
22	Ti	47.88	69	Tm	168.934
23	V	50.9415	70	Yb	173.04
24	Cr	51.996	71	Lu	174.967
25	Mn	54.9380	72	Hf	178.49
26	Fe	55.847	73	Ta	180.948
27	Co	58.9332	74	W	183.85
28	Ni	58.69	75	Re	186.207
29	Cu	63.546	76	Os	190.2
30	Zn	65.39	77	Ir	192.22
31	Ga	69.72	78	Pt	195.08
32	Ge	72.59	79	Au	196.967
33	As	74.9216	80	Hg	200.59
34	Se	78.96	81	Tl	204.383
35	Br	79.904	82	Pb	207.2
36	Kr	83.80	83	Bi	208.980
37	Rb	85.4678	84	Po	(209) ^a
38	Sr	87.62	85	At	(210) ^a
39	Y	88.9059	86	Rn	(222) ^a
40	Zr	91.224	87	Fr	(223) ^a
41	Nb	92.9064	88	Ra	226.025
42	Mo	95.94	89	Ac	227.028
43	Tc	(98) ^a	90	Th	232.038
44	Ru	101.07	91	Pa	231.036
45	Rh	102.906	92	U	238.029
46	Pd	106.42	93	Np	(237) ^a
47	Ag	107.868	94	Pu	(239) ^a

^aMass number of longest-lived isotope in nature.

both Ba^{2+} and SO_4^{2-} is also 9.512×10^{-6} mol/L. The concentration of Ba^{2+} in 1 L of saturated barite solution can also be expressed as:

$$9.512 \times 10^{-6} \times 137.33 = 1.306 \times 10^{-3} \text{ g/L}$$

Alternatively, we calculate the number of Ba^{2+} ions in one liter of a saturated barite solution by means of Avogadro's number:

$$\begin{aligned} 9.512 \times 10^{-6} \times 6.022045 \times 10^{23} \\ = 5.728 \times 10^{18} \text{ ions/L} \end{aligned}$$

Such computations involving conversions of amounts of elements or compounds in grams to the corresponding number of moles by means of the atomic or molecular weights occur commonly in geochemistry.

Before we close this chapter we define the gram-equivalent weight.

A gram-equivalent weight of an ion is the gram-atomic or gram-molecular weight divided by the valence. For acids and bases the gram-equivalent weight is the gram-molecular weight of the compound divided by the number of hydrogen ions or hydroxyl ions the acid or base can produce when dissolved in water.

Equivalent weights are used in geochemistry when electrical charges of ions are an important consideration. In addition, they are traditionally used to express the concentrations of acids or bases in a way that indicates the concentrations of hydrogen or hydroxyl ions that may be available for reaction.

In practice, the equivalent weight of an element is calculated by dividing its atomic weight by the charge the atoms of that element acquire when the element is dissolved in water. Therefore, the equivalent weight of a divalent element like calcium is equal to the atomic weight divided by two. Conversely, one mole of Ca^{2+} contains two equivalents of Ca^{2+} . In the case of molecules of an acid such as H_2SO_4 , the equivalent weight is equal to one half of the molecular weight because one mole of H_2SO_4 contains two equivalents of hydrogen ions. Similarly, phosphoric acid (H_3PO_4) can yield three moles

of hydrogen ions per mole of the compound, and therefore its equivalent weight is equal to its molecular weight divided by three. In this case, it makes no difference that phosphoric acid actually gives up its hydrogen ions reluctantly and releases all three of them only under special conditions.

6.5 Summary

The periodic table was originally invented by D. I. Mendeleev and other chemists in the 19th century based on the relationship between the atomic weights of the elements and their chemical and physical properties. We now know that these relationships are caused by the composition of the nuclei of the atoms and by the distribution of their electrons in the available orbitals.

The so-called long form of the periodic table is organized into seven horizontal rows called periods and eighteen vertical columns called groups. The physical and chemical properties of elements in the periods change systematically with increasing atomic number. The elements in the groups tend to have similar properties because they have similar electronic structures.

The concept of the atomic weight is now based on the masses and abundances of the naturally occurring isotopes of the elements. The atomic weights are used to define the gram-atomic weight of elements or the gram-molecular weight of compounds, also known collectively as the mole. The importance of the mole in chemistry arises from the fact that one mole of an element or compound always contains the same number of atoms or molecules. This number is known as Avogadro's number.

Chemical reactions are represented by equations in which the quantities of reactants and products are specified in terms of moles, which can be converted to the numbers of atoms or molecules by virtue of Avogadro's number.

The gram-equivalent weight takes into account the electrical charges of ions or the number of hydrogen or hydroxyl ions that acids or bases can release into an aqueous solution.

Problems

1. Familiarize yourself with the names, atomic numbers, and positions in the periodic table of the elements having atomic numbers from 1 to 36.

2. Calculate the atomic weight of magnesium given the abundances and masses of its naturally occurring isotopes.

	Abundance, %	Mass, amu
$^{24}_{12}\text{Mg}$	78.99	23.985 042
$^{25}_{12}\text{Mg}$	10.00	24.985 837
$^{26}_{12}\text{Mg}$	11.01	25.982 593

(Answer: 24.305)

3. Calculate the formula weight of orthoclase feldspar (KAlSi_3O_8) using the atomic weights in Table 6.2.

(Answer: 278.332)

4. How many moles of Na^+ are present in one liter of an aqueous solution of Na_2SO_4 containing 4.760 g of the compound?

(Answer: 0.0670 mol)

5. What is the weight of one atom of $^{238}_{92}\text{U}$ in grams given that the mass of this isotope is 238.050 784 amu?

(Answer: 3.953×10^{-22} g)

6. How many atoms of iron are present in 5.00 g of hematite (Fe_2O_3)?

(Answer: 3.77×10^{22} atoms)

7. What is the concentration of Cr in the mineral chromite (FeCr_2O_4)?

(Answer: 46.5%)

8. If the concentration of SO_4^{2-} is 2.5×10^{-3} mol/L, how many grams of SO_4^{2-} are present in one liter?

(Answer: 0.24 g)

9. A solution of $\text{Al}_2(\text{SO}_4)_3$ contains 2×10^{-4} mol/L of Al^{3+} . How many grams of SO_4^{2-} does it contain per liter?

(Answer: 0.029 g/L)

10. How many gram-equivalent weights of Al^{3+} and SO_4^{2-} are in 2 mol of $\text{Al}_2(\text{SO}_4)_3$?

(Answer: Al^{3+} : 12; SO_4^{2-} : 12)

References

- ASIMOV, I., 1965. *A Short History of Chemistry*. Doubleday, Garden City, NY, 263 pp.
- FAURE, G., 1986. *Principles of Isotope Geology*. 2nd ed. Wiley, New York, 589 pp.
- GREENWOOD, N. N., and A. EARNshaw, 1984. *Chemistry of the Elements*. Pergamon Press, Oxford, England, 1542 pp.
- MAZURS, E. G., 1974. *Graphic Representation of the Periodic System During One Hundred Years*. University of Alabama Press, Tuscaloosa.
- VAN SPROSEN, J. W., 1969. *The Periodic System of the Elements*. Elsevier, Amsterdam, 368 pp.
- WEAST, R. C., M. J. ASTLE, and W. H. BEYER, 1986. *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton, FL.
- WEEKS, M. E., 1956. *Discovery of the Elements*, 6th ed. J. Chem. Ed. Pub., 910 pp.

Chemical Bonds, Ionic Radii, and Crystals

The physical and chemical properties of the elements vary with increasing atomic number in accordance with the *periodic law*. Some of these properties are neatly summarized in periodic tables available in university book stores. It will be helpful to use such a table to study the topics presented in this chapter.

7.1 Electron Donors Versus Acceptors

We can divide the elements in the periodic table into two groups based on their tendency to give up electrons or to attract them. In general, the elements on the left side of the periodic table are the *electron donors* because their electronic orbitals are largely empty. The elements on the right side of the periodic table have orbitals that are nearly full, which causes them to be *electron acceptors*. The elements that are located between the alkali metals on the left and the halogens on the right vary progressively in their tendencies to be electron donors or acceptors, depending on how close they are to filling their orbitals with electrons. The electron donors are the *metals*, whereas the electron acceptors are the *non-metals*. The metallic character of the elements generally decreases from left to right in the periods as the orbitals are filling up with electrons.

The properties of metals and nonmetals are complementary in the sense that the electrons given up by metallic elements are picked up by

the nonmetals. If a complete transfer of electrons is achieved, the electron-donor atoms become positively charged ions called *cations*, whereas the electron-acceptor atoms acquire a negative charge and form *anions*. Oppositely charged ions are attracted to each other and may form an electrostatic or *ionic bond*. Most minerals are chemical compounds composed of cations (metals) and anions (nonmetals) held together by ionic bonds.

When two elements having similar metallic or nonmetallic character interact, electrons are not actually transferred, but are shared by the atoms. The sharing of electrons among the atoms of two or more different elements establishes a *covalent bond* between them. The elements do not necessarily share the electrons equally, which causes covalent bonds to have a certain amount of ionic character. Similarly, the transfer of electrons among atoms of elements on opposite sides of the periodic table is never complete. As a result, ionic bonds have covalent character whose magnitude depends on the difference in the tendency of the atoms to attract electrons to themselves. As atoms become more equal in their ability to attract electrons, the covalent character of the bond increases. The distinction between ionic and covalent bonds is therefore an over-simplification of a very complex interaction among atoms of different elements (Pauling, 1960). The only truly covalent bonds occur when two atoms of the same element combine to form diatomic molecules such as H_2 , O_2 , or N_2 .

7.2 Measures of Metallic Character

Although we can appreciate the difference between electron donors and electron acceptors *qualitatively*, we need to measure these tendencies *quantitatively* in order to be able to predict what kind of a bond the atoms of two elements are likely to form. Several parameters have been defined that, in fact, permit us to do this. They are identified and defined as follows.

First ionization potential is the energy required to remove one electron from a neutral atom in a vacuum and to place it at rest an infinite distance away.

Electronegativity is a measure of the ability of an atom in a molecule to attract electrons to itself (Pauling, quoted in Cotton and Wilkinson, 1962, p. 89).

Standard electrode potential is the voltage generated when one mole of electrons is removed from one mole of an element or ion "in the standard state."

We deal with the standard electrode potential in Section 14.3 and consider here how the first ionization potentials and the electronegativities can be used to compare the metallic character of different elements.

The first ionization potential indicates how strongly the nucleus of a neutral atom attracts an electron in a partially filled orbital. Figure 7.1A indicates that the first ionization potentials *increase* with increasing atomic number in each period. The increase coincides with the progressive filling of the electronic orbitals and reflects the reluctance of atoms to give up electrons from orbitals that are nearly full. For example, we see that in periods 2 and 3 the first ionization potentials increase sharply with increasing atomic number toward the noble gas elements that terminate each period. We can even recognize the effect on the first ionization potential of filling the *s*-orbitals or half-filling the *p*-orbitals. This explains why the first ionization potential of B is less than that of Be and why it takes less energy to remove an electron from O than from N. The

same effect can be seen in period 3 in the first ionization potentials of Mg and Al and of P and S.

The first ionization potentials of the transition metals of period 4, which have partially filled *3d* orbitals, vary much *less* than those in the first three periods. Period 4 starts out well enough with K and Ca, but then the first ionization potentials change little as we complete the sequence ending with Zn. Gallium starts to fill the *4p* orbitals, which causes it to have a lower ionization potential than Zn. However, the first ionization potentials then rise rapidly with increasing atomic number until period 4 ends with Kr. The next period, 5, starting with Rb and ending with Xe, likewise illustrates the lack of differentiation among the elements with electrons in the *4d* orbitals. The first ionization potentials for these and all other elements are listed in Table 7.1.

Evidently, the systematic variation of the first ionization potentials confirms that the *metallic character* of the elements in each period *decreases* with *increasing* atomic number. The first ionization potentials even reflect the reduction in the energy of atoms that have completely filled or half-filled orbitals and, in general, permit us to rank the elements throughout the periodic table in terms of their metallic character, which arises from their tendency to be electron donors.

Ionization potentials required to remove additional electrons rise to high values because it takes extraordinary amounts of energy to remove electrons from atoms that have acquired a positive charge because they have already lost one electron or because the remaining electrons completely fill the orbital they occupy. Therefore, during chemical reactions in nature elements generally lose only their "valence electrons," that is, those that reside outside of filled orbitals.

The problem with ionization potentials as predictors of chemical properties is that the chemical reactions we want to study do not occur in a vacuum but take place in mixtures of gases, in aqueous solutions, in silicate melts, and even in the solid state. Therefore, we need a parameter that is appropriate for the environments in which chemical reactions actually take place.

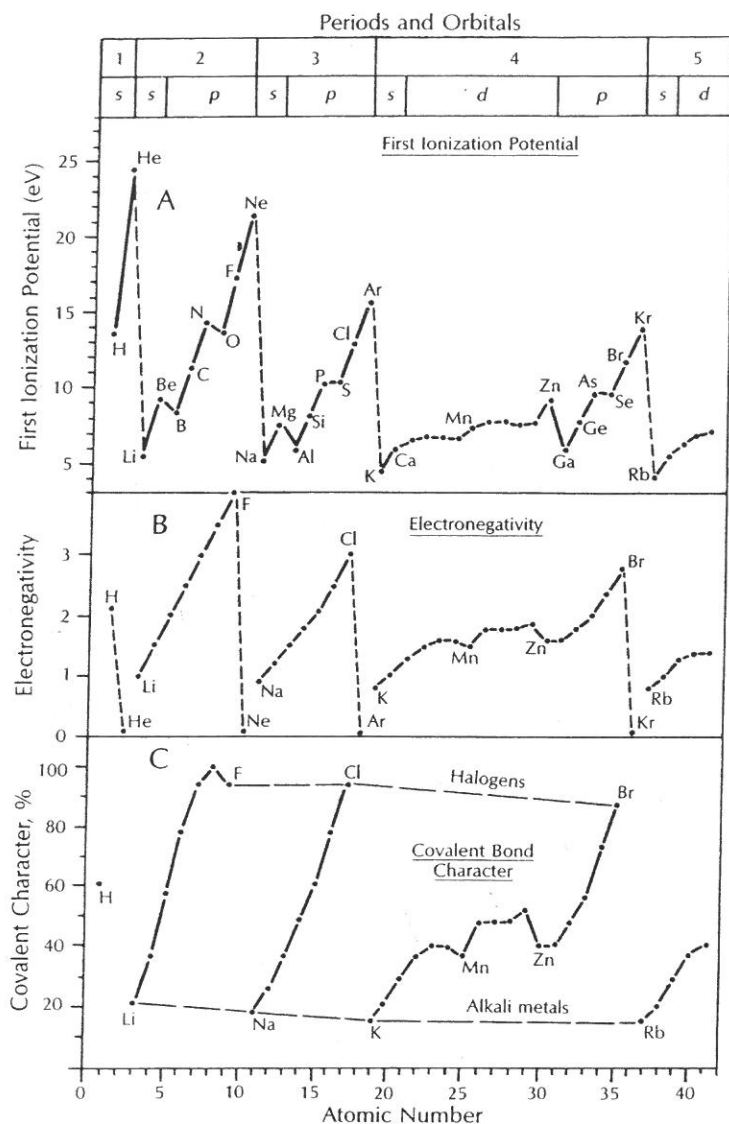


Figure 7.1 A: Variation of the first ionization potential with increasing atomic number in the first four periods. The first ionization potentials increase as the electronic orbitals are filling up in each period. Note that Be and N have exceptionally high ionization potentials consistent with filling or half-filling of electronic orbitals. The ionization potentials of elements in period 4 with partially filled *d*-orbitals vary little with atomic number. In general, the data show that the character of the elements in each period changes from metallic (low ionization potential, hence electron donor) to nonmetallic (high ionization potential, hence electron acceptor).

B: Variation of the electronegativity of the elements with increasing atomic number. The diagram shows that the electronegativity increases as the available orbitals become filled with electrons. This pattern, therefore, reflects the increasing tendency of elements in the periods to fill their orbitals by attracting electrons to themselves. Note that metallic elements have low electronegativities, whereas nonmetallic elements have high values. Therefore, the electronegativities also reflect the progressive decrease of the metallic character of elements with increasing atomic number in each period.

C: Variation of the covalent character of single bonds with oxygen based on electronegativity differences (Table 7.2). As the elements lose their metallic character and become increasingly reluctant electron donors, the bonds they form with oxygen are increasingly covalent in character. In general, the alkali metal–oxygen bonds are highly ionic, whereas the halogen–oxygen bonds are highly covalent. All other elements in the periodic table form bonds with oxygen whose character is intermediate between these extremes.

The electronegativities, proposed by Pauling (1960), are a set of dimensionless numbers calculated from the known strengths of bonds between atoms in molecules. They are a measure of the ionic character of covalent bonds and therefore indicate the extent to which two atoms in a molecule actually share their valence electrons equally. Elements having a low electronegativity act as electron donors, whereas elements with high electronegativity act as electron acceptors. Cesium has the lowest electronegativity (0.7) and therefore has the strongest tendency to be an electron donor, whereas fluorine has the highest elec-

tronegativity (4.0) and is the strongest electron acceptor. The electronegativities of all naturally occurring elements are listed in Table 7.1 and are displayed in Figure 7.1B.

As expected, we find that the electronegativities rise with increasing atomic number in each period. The electronegativities of the noble gases are shown as “zero” because these elements do not attract electrons to themselves. The alkali metals and the halogens demonstrate that the electronegativities of group A elements *decrease* with increasing atomic number. The first ionization potentials of these elements also decrease with

Table 7.1 First Ionization Potentials and Electronegativities of the Elements

<i>Z</i>	<i>Element</i>	<i>First ionization potential,^a eV</i>	<i>Electronegativity^b</i>	<i>Z</i>	<i>Element</i>	<i>First ionization potential,^a eV</i>	<i>Electronegativity^b</i>
1	H	13.598		48	Cd	8.993	1.7
2	He	24.587	2.1	49	In	5.786	1.7
3	Li	5.392	1.0	50	Sn	7.344	1.8
4	Be	9.322	1.5	51	Sb	8.641	1.9
5	B	8.298	2.0	52	Te	9.009	2.1
6	C	11.260	2.5	53	I	10.451	2.5
7	N	14.534	3.0	54	Xe	12.130	
8	O	13.618	3.5	55	Cs	3.894	0.7
9	F	17.422	4.0	56	Ba	5.212	0.9
10	Ne	21.564		57	La	5.577	1.1
11	Na	5.139	0.9	58	Ce	5.47	1.1
12	Mg	7.646	1.2	59	Pr	5.42	1.1
13	Al	5.986	1.5	60	Nd	5.49	1.2
14	Si	8.151	1.8	61	Pm	5.55	
15	P	10.486	2.1	62	Sm	5.63	1.2
16	S	10.360	2.5	63	Eu	5.67	
17	Cl	12.967	3.0	64	Gd	6.14	1.1
18	Ar	15.759		65	Tb	5.85	1.2
19	K	4.341	0.8	66	Dy	5.93	
20	Ca	6.113	1.0	67	Ho	6.02	1.2
21	Sc	6.54	1.3	68	Er	6.10	1.2
22	Ti	6.82	1.5	69	Tm	6.18	1.2
23	V	6.74	1.6	70	Yb	6.254	1.1
24	Cr	6.766	1.6	71	Lu	5.426	1.2
25	Mn	7.435	1.5	72	Hf	7.0	1.3
26	Fe	7.870	1.8	73	Ta	7.89	1.5
27	Co	7.86	1.8	74	W	7.98	1.7
28	Ni	7.635	1.8	75	Re	7.88	1.9
29	Cu	7.726	1.9	76	Os	8.7	2.2
30	Zn	9.394	1.6	77	Ir	9.1	2.2
31	Ga	5.999	1.6	78	Pt	9.0	2.2
32	Ge	7.899	1.8	79	Au	9.225	2.4
33	As	9.81	2.0	80	Hg	10.437	1.9
34	Se	9.752	2.4	81	Tl	6.108	1.8
35	Br	11.814	2.8	82	Pb	7.416	1.8
36	Kr	13.999		83	Bi	7.289	1.9
37	Rb	4.177	0.8	84	Po	8.42	2.0
38	Sr	5.695	1.0	85	At		2.2
39	Y	6.38	1.3	86	Rn	10.748	
40	Zr	6.84	1.4	87	Fr		0.7
41	Nb	6.88	1.6	88	Ra	5.279	0.9
42	Mo	7.099	1.8	89	Ac	6.9	1.1
43	Tc	7.28	1.9	90	Th		1.3
44	Ru	7.37	2.2	91	Pa		1.5
45	Rh	7.46	2.2	92	U		1.7
46	Pd	8.34	2.2	93	Np		1.3
47	Ag	7.576	1.9	94	Pu	5.8	1.3

^aWeast et al. (1986).^bPauling (1960)

increasing atomic number in each group. This indicates that the *binding energy* of the first valence electron of elements in a given group decreases as the volume of the atoms in that group increases. In other words, the larger an atom, the more loosely it holds its valence electrons. Consequently, the metallic character of the group A elements *increases* with increasing atomic number.

In the B groups, where *d*- and *f*-orbitals are being filled, the electronegativities change much less dramatically with increasing atomic number than they do in the A groups. As a result, the chemical properties of these elements are more uniform than those of the elements in the A groups. Moreover, the electronegativities of elements in B groups do not decrease with increasing atomic number as they generally do in the A groups. For example, the electronegativities of the congeners of group VIIIB (Fe, Co, and Ni) actually rise with increasing atomic number.

The concept of electronegativity has merit because the *differences* in the electronegativities of elements are related to the ionic character of the bond formed by their atoms. Accordingly, two elements with similar electronegativities form covalent bonds with little ionic character, whereas elements having different electronegativities form bonds whose ionic character is proportional to the magnitude of the electronegativity difference. The relationship between the electronegativity difference and the ionic character of chemical bonds is expressed quantitatively by the data in Table 7.2. In Figure 7.1C we see how the bond character varies with increasing atomic number when elements form bonds with oxygen. Note that the graph shows the percent *covalent* character in order to emphasize the relationship between bond character and electronegativity (Figure 7.1B) or first ionization potential (Figure 7.1A). We see that the oxygen bonds of the elements become increasingly covalent in each period. The halogens form the most covalent oxygen bonds, whereas the alkali metals form oxygen bonds that are largely ionic. The transition metals in the fourth period show less variation in bond character than elements with valence electrons in *s*- and *p*-orbitals.

The data in Tables 7.1 and 7.2 permit us to predict the ionic character of the bond between any two elements in the periodic table. In general, we find that bonds between neighboring elements in the periodic table are highly covalent. For example, the nonmetals on the right side of the periodic table form many familiar compounds and anion complexes that are covalently bonded. The H—O bond in the H₂O, the C—O bond in CO₃²⁻, the N—O bond in NO₃⁻, the S—O bond in SO₄²⁻, and the Si—O bond in SiO₄⁴⁻ are all strongly covalent.

In addition, we can demonstrate that bonds between elements from opposite ends of the periodic table are highly ionic. The best examples are the alkali halides (e.g., NaCl, KCl, and CsF). In fact, the Cs—F bond is the most ionic bond we know because Cs has the strongest tendency to be an electron donor (lowest electronegativity) and F is the strongest electron acceptor (highest electronegativity). Bonds with well-developed ionic character also occur between the cations of metals and complex anions exemplified by CaCO₃, NaNO₃, MgSO₄, and Fe₂SiO₄, all of which occur naturally as minerals.

Although the electronegativities of complex anions are not defined, we nevertheless know that the bonds between the cation of the metals and the complex anions are highly ionic because these compounds dissociate into ions when they dissolve in water.

7.3 Bonding in Molecules

We now come to the question: What difference does it make in geochemistry whether chemical bonds are covalent or ionic? The answer is that the physical and chemical properties of all compounds depend on the character of the bonds that hold them together.

An important property of most minerals is that they dissociate into ions when they dissolve in water. For example, when calcite (CaCO₃) dissolves in water, it forms Ca²⁺ ions and CO₃²⁻ ions:



Table 7.2 Percent Ionic Character of a Single Chemical Bond with Oxygen

<i>Difference in electronegativity</i>	<i>Ionic character, %</i>	<i>Difference in electronegativity</i>	<i>Ionic character, %</i>
0.1	0.5	1.7	51
0.2	1	1.8	55
0.3	2	1.9	59
0.4	4	2.0	63
0.5	6	2.1	67
0.6	9	2.2	70
0.7	12	2.3	74
0.8	15	2.4	76
0.9	19	2.5	79
1.0	22	2.6	82
1.1	26	2.7	84
1.2	30	2.8	86
1.3	34	2.9	88
1.4	39	3.0	89
1.5	43	3.1	91
1.6	47	3.2	92

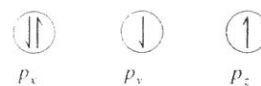
SOURCE: Sargent-Welch (1980).

The carbonate anion does *not* dissociate into carbon and oxygen ions because the C — O bonds are highly covalent, whereas the Ca—CO₃ bond is largely ionic. Why should that make a difference? The answer has to do with the interactions between the molecules of the solvent (water in this case) and the calcite “molecules.”

The H—O bond in the water molecule is about 60% covalent as can be seen from Figure 7.1C. In addition, the electronegativity of oxygen (3.5) is larger than that of hydrogen (2.1). Consequently, we conclude that O attracts the electrons of the H atoms to itself. The unequal sharing of the electron between H and O therefore causes a net negative charge to develop on the O atoms of water molecules, whereas the H atoms have a net positive charge. In other words, the water molecule has

electrical polarity and is therefore said to be “polar.”

The manner in which the covalent H—O bonds form also determines the shape of the water molecule. A quick review of the electronic structure of O indicates that it has four electrons in the 2*p* orbitals, whereas H has one electron in the 1*s* orbital. The bond between them forms by sharing of the *unpaired* electrons. In accordance with rule 3 of the Aufbau principle (Chapter 5), one of the *p*-orbitals of oxygen contains two electrons with paired spins, whereas the other two *p*-orbitals of oxygen contain one electron each. We can represent the *p*-orbitals of oxygen as circles and the electrons they contain by arrows that point up or down depending on the spin.



The angle between these p -orbitals of oxygen is 90° because they are symmetrical about the x -, y -, and z -axes. Therefore, we expect that the angle between the H—O bonds in the water molecule should also be 90° . However, the observed angle is 104.45° (Fyfe, 1964).

The discrepancy arises because the s - and p -orbitals of O are merged in such a way that the angles between the “hybridized” orbitals are no longer 90° . Hybridization of orbitals is a common phenomenon in covalently bonded molecules and is the key to understanding the shapes or *stereochemistry* of covalently bonded molecules (Greenwood and Earnshaw, 1984; Pauling, 1960).

The polarity of the water molecule therefore arises not only because of the unequal sharing of the electrons between H and O but also because one of the hybridized p -orbitals of O containing the two paired electrons points away from the other two, which are involved in the bonding. In addition, the H_2O molecule is inherently polar because the O atom has more electrons than the H atoms.

Because of their electrical polarity, water molecules are attracted to electrical charges on the surface of an ionic crystal such as CaCO_3 . The resulting electrostatic interactions weaken the ionic bonds between the Ca^{2+} and the CO_3^{2-} ions, but have no effect on the covalent C—O bonds of the carbonate ions.

The ions that form by dissociation attract water molecules to themselves and thereby become “hydrated.” The number of water molecules bound to an ion depends primarily on its radius but also on its charge. For example, Be^{2+} (radius = $0.35 \text{ \AA}$; Ahrens, 1952) holds four water molecules to form the hydrated ion $\text{Be}(\text{OH}_2)_4^{2+}$ whereas Al^{3+} (radius = $0.51 \text{ \AA}$) holds six water molecules and forms $\text{Al}(\text{OH}_2)_6^{3+}$. Note that we represent the hydrated Be^{2+} ion as $\text{Be}(\text{OH}_2)_4^{2+}$ because the Be^{2+} is attracted to the negatively charged O atoms of the water molecule. Anions are also hydrated by attracting the positively charged hydrogen atoms of water. In some cases the water molecules are held so

strongly that they are incorporated into crystals as water of hydration, as, for example, in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum).

Therefore, the answer to the original question is that water is able to dissolve ionic solids because it dissociates them into ions, which are then separated from each other by becoming hydrated. However, covalent bonds do not dissociate in water or in other polar solvents. Therefore, water is generally not an effective solvent for covalently bonded compounds.

7.4 Ionic Crystals

When ions come together to form a crystal they assemble in regular patterns dictated by the requirement of “closest packing.” This requirement arises because the strength of the electrostatic bond (F) between cations and anions is inversely proportional to the square of the distance (r) between them:

$$F = \frac{e_1 e_2}{r^2} \quad (7.2)$$

where e_1 and e_2 are the charges of the ions. Evidently, the magnitude of F increases as r decreases. Therefore, the ions in a crystal arrange themselves in such a way that the interionic distances are minimized, hence the tendency for closest packing. In this context, ions are assumed to be incompressible spheres like billiard balls.

A second requirement is that crystals must be electrically neutral. This requirement determines the ratio of cations to anions and is reflected in the chemical formulas of minerals. In addition, the requirement for electrical neutrality must be obeyed whenever substitutions occur in ionic crystals.

The arrangement of ions in a crystal can be understood in terms of the magnitudes of the radii of the cations and anions expressed by the *radius ratio*, which is defined as the ratio of the radius of the cation to that of the anion. In calculating radius ratios one commonly uses O^{2-} as the anion

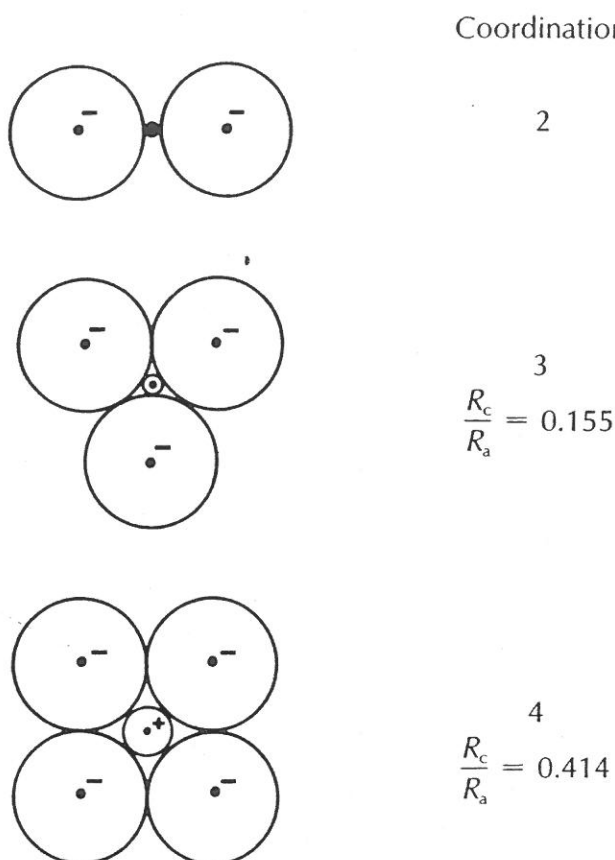


Figure 7.2 Examples of closest packing of anions around cations at increasing values of the radius ratio. When $R_c/R_a > 0.155$, three anions fit around the cation and when $R_c/R_a > 0.414$, fourfold coordination occurs. Coordination numbers 6, 8, and 12 are also important in mineral structures and are pictured in Figure 7.4.

because oxygen is the most abundant chemical element in the crust of the Earth.

The geometrical arrangements of ions in a crystal are described by the *coordination number*, which is the number of anions that surround a particular cation in an ionic crystal. It turns out that the coordination numbers of elements in ionic crystals can be predicted based on their radius ratios. We see from Figure 7.2 that only two large anions can fit around a very small cation. The smallest coordination number therefore is 2. If the cation is larger than in the case just considered and the radius ratio exceeds a critical value,

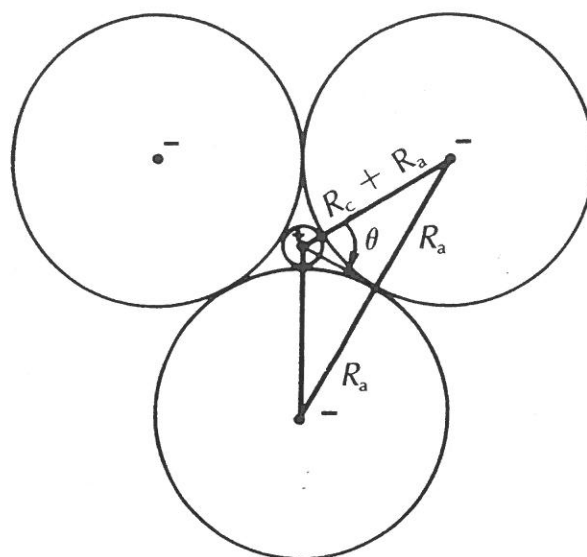


Figure 7.3 Derivation of the critical radius ratio for threefold coordination. R_c and R_a are the ionic radii of the cation and anion, respectively. The critical relationship is $\sin 60^\circ = R_a/(R_c + R_a)$ from which it follows that $R_c/R_a = 0.155$.

the coordination number rises to 3. At a still higher value of the radius ratio, four anions can be packed around the cation.

The critical value of the radius ratio at which threefold coordination is possible in a planar structure can be derived from geometrical considerations pictured in Figure 7.3. Let R_c and R_a be the radii of the cation and anion, respectively. By examining Figure 7.3 we find that:

$$\sin \theta = \frac{R_a}{R_c + R_a} \quad (7.3)$$

since $\theta = 60^\circ$ and $\sin 60^\circ = 0.8660$:

$$\frac{R_a}{R_c + R_a} = 0.8660 \quad (7.4)$$

By cross multiplying and collecting terms we obtain:

$$\frac{R_c}{R_a} = \frac{0.134}{0.866} = 0.155 \quad (7.5)$$

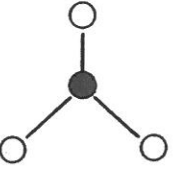
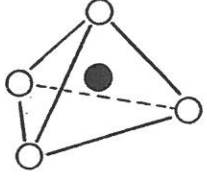
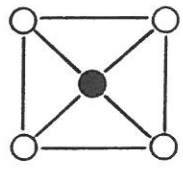
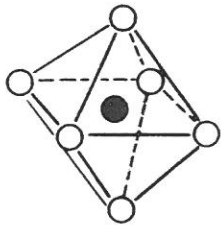
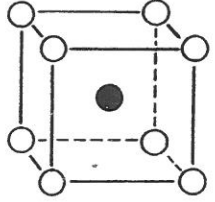
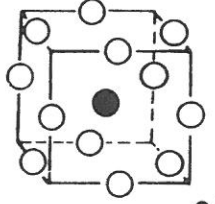
Therefore, threefold coordination becomes possible in a planar structure when the radius ratio is

equal to or greater than 0.155. A similar argument indicates that fourfold coordination occurs when the radius ratio is 0.414.

All of the packing arrangements shown in Figure 7.2 are two dimensional or planar. Since crystals are actually three-dimensional bodies, we must also consider three-dimensional patterns of fitting anions around cations. For example, fourfold coordination occurs when the anions occupy the corners of a tetrahedron with the cation in its center. Similarly, sixfold coordination is realized in an octahedron where six anions occupy the corners and the cation resides in the center. Higher coordination numbers of 8 and 12 are common and involve the cubic structures shown in Figure 7.4. Other coordination numbers, for example, 5, 7, 9, 10, and 11, occur only rarely and are not important in the crystal structures of minerals (Fyfe, 1964).

7.5 Ionic Radii

The radii of ions in crystals were first determined by V. M. Goldschmidt and Linus Pauling in the late 1920s by means of x-ray diffraction and are expressed in angstroms ($\text{\AA}$; $1\text{\AA} = 10^{-10}\text{ m}$). Ionic radii are determined from the distances between ions in crystals and depend on the structure of the crystal in which they were measured. Most ionic radii were originally derived from crystals in which each cation is surrounded by six anions (Heydemann, 1969). A complete set of such radii was published by Ahrens (1952), but these have now been superseded by the work of Shannon and Prewitt (1969). Subsequently, Whittaker and Muntus (1970) published a new set of ionic radii (listed in Table 7.3) that takes into account the different coordination numbers that may occur in different kinds of crystals. Another set of radii was later published by Shannon (1976). The dependence of ionic radii on the coordination number occurs because the electron cloud of an ion can be deformed by the electrical charges that surround it in a crystal lattice. For example, the radius of Na^+ varies from 1.07 to 1.40 $\text{\AA}$

Radius ratio	Coordination	Arrangement of ions
<0.155	2	 Linear
$0.155-0.225$	3	 Trigonal planar
$0.225-0.414$	4	 Tetrahedral
$0.414-0.732$	4	 Square planar
$0.414-0.732$	6	 Octahedral
$0.732-1.00$	8	 Body-centered cubic
>1.00	12	 Edge-centered cubic

● Cation, ○ Anion

Figure 7.4 Possible arrangements of ions in crystals for limiting values of the radius ratios and different values of the coordination number.

Table 7.3 Radii of the Ions of the Elements in Angstrom Units (Å) for Different Charges and Coordination Numbers

Z	Symbol	Valence	Coordination numbers									
			II	III	IV ^a	V	VI ^{a,b}	VII	VIII	IX	X	XII
1	H	+1					extremely small					
3	Li	+1			0.68		0.82					
4	Be	+2		0.25	0.35							
5	B	+3		0.10	0.20							
6	C	+4					2.60 (P)					
		+4					0.16 (A)					
7	N	+3					0.16 (A)					
		+5					0.13 (A)					
8	O	+2	1.27	1.28	1.30		1.32		1.34			
9	F	+1	1.21	1.22	1.23		1.25					
11	Na	+1			1.07	1.08	1.10	1.21	1.24	1.40		
12	Mg	+2			0.66	0.75	0.80		0.97			
13	Al	+3			0.47	0.56	0.61					
14	Si	+4			0.34		0.48					
15	P	+3					0.44 (A)					
		+5			0.25		0.35 (A)					
16	S	+2			1.56		1.72		1.78			
		+6			0.20		0.30 (A)					
17	Cl	+1			1.67		1.72		1.65			
		+5		0.20			0.34 (A)					
		+7			0.28		0.27 (A)					
19	K	+1					1.46	1.54	1.59	1.63	1.67	1.68
20	Ca	+2					1.08	1.15	1.20	1.26	1.36	1.43
21	Sc	+3					0.83		0.95			
22	Ti	+2					0.94					
		+3					0.75					
		+4				0.61	0.69					
23	V	+2					0.87					
		+3					0.72					
		+4					0.67					
		+5			0.44	0.54	0.62					
24	Cr	+2					0.81 (L)					
							0.90 (H)					
		+3					0.70					
		+4			0.52		0.63					
		+5			0.43							
		+6			0.38		0.52 (A)					
25	Mn	+2					0.75 (L)			1.01		
							0.92 (H)					
		+3				0.66	0.66 (L)					
							0.73 (H)					
		+4					0.62					
		+6			0.35							
		+7			0.34		0.46 (A)					

Table 7.3 (continued)

Z	Symbol	Valence	Coordination numbers									
			II	III	IV ^a	V	VI ^{a,b}	VII	VIII	IX	X	XII
26	Fe	+2			0.71 (H)		0.69 (L) 0.86 (H)					
		+3			0.57 (H)		0.63 (L) 0.73 (H)					
27	Co	+2			0.65 (H)		0.73 (L) 0.83 (H)					
		+3					0.61 (L) 0.69 (H)					
28	Ni	+2					0.77					
		+3					0.64 (L) 0.68 (H)					
29	Cu	+1	0.54									
		+2			0.70	0.73	0.81					
30	Zn	+2			0.68	0.76	0.83		0.98			
31	Ga	+3			0.55	0.63	0.70					
32	Ge	+4			0.48		0.62					
33	As	+5			0.42		0.58					
34	Se	-2					1.88		1.90			
		+6			0.37		0.42 (A)					
35	Br	-1			1.88		1.95 (P)		1.84			
		+7			0.34		1.39 (A)					
37	Rb	+1					1.57	1.64	1.68		1.74	1.81
38	Sr	+2					1.21	1.29	1.33		1.40	1.48
39	Y	+3					0.98		1.10	1.18		
40	Zr	+4					0.80	0.86	0.92			
41	Nb	+2					0.79					
		+3					0.78					
		+4					0.77					
		+5			0.40		0.72	0.74				
42	Mo	+3					0.75					
		+4					0.73					
		+5					0.71					
		+6			0.50	0.58	0.68	0.79				
43	Tc	+4					0.72					
44	Ru	+3					0.76					
		+4					0.70					
45	Rh	+3					0.75					
		+4					0.71					
46	Pd	+1	0.67									
		+2			0.72		0.94					
		+3					0.84					
		+4					0.70					
47	Ag	+1	0.75		1.10	1.20	1.23	1.32	1.38			
		+3			0.73							
48	Cd	+2			0.88	0.95	1.03	1.08	1.15			1.39
49	In	+3					0.88		1.00			
50	Sn	+2					0.93 (A)		1.30			
		+4					0.77					

Table 7.3 (continued)

Z	Symbol	Valence	Coordination numbers									
			II	III	IV ^a	V	VI ^{a,b}	VII	VIII	IX	X	XII
51	Sb	+3			0.85	0.88	0.76 (A)					
		+5					0.69					
52	Te	+4		0.60			0.70 (A)					
		+6					0.56 (A)					
53	I	+1					2.13		1.97			
		+5					1.03					
55	Cs	+1					1.78		1.82	1.86	1.89	1.96
56	Ba	+2					1.44	1.47	1.50	1.55	1.60	1.68
57	La	+3					1.13	1.18	1.26	1.28	1.36	1.40
58	Ce	+3					1.09		1.22	1.23		1.37
		+4					0.88		1.05			
59	Pr	+3					1.08		1.22			
		+4					0.86		1.07			
60	Nd	+3					1.06		1.20	1.17		
61	Pm	+3					1.04					
62	Sm	+3					1.04		1.17			
63	Eu	+2					1.25		1.33			
		+3					1.03	1.11	1.15			
64	Gd	+3					1.02	1.12	1.14			
65	Tb	+3					1.00	1.10	1.12			
		+4					0.84		0.96			
66	Dy	+3					0.99		1.11			
67	Ho	+3					0.98		1.10			
68	Er	+3					0.97		1.08			
69	Tm	+3					0.96		1.07			
70	Yb	+3					0.95		1.06			
71	Lu	+3					0.94		1.05			
72	Hf	+4					0.79		0.91			
73	Ta	+3					0.75					
		+4					0.74					
		+5					0.72		0.77			
74	W	+4					0.73					
		+6			0.50		0.68					
75	Re	+4					0.71					
		+5					0.60					
		+6					0.60					
		+7			0.48		0.65					
76	Os	+4					0.71					
77	Ir	+3					0.81					
		+4					0.71					
78	Pt	+2			0.68		0.80 (A)					
		+4					0.71					
79	Au	+1					1.37 (A)					
		+3			0.78		0.85 (A)					
80	Hg	+1		1.05								
		+2	0.77		1.04		1.10		1.22			
81	Tl	+1					1.58		1.68			1.84
		+3					0.97		1.08			

Table 7.3 (continued)

Z	Symbol	Valence	Coordination numbers									
			II	III	IV ^a	V	VI ^{a,b}	VII	VIII	IX	X	XII
82	Pb	+2 ^c			1.02		1.26		1.37	1.41		1.57
		+4					0.86		1.02			
83	Bi	+3				1.07	1.10		1.19			
84	Po	+4							1.16			
		+6					0.67 (A)					
85	At	+7					0.62 (A)					
86	Fr	+1					1.80 (A)					
87	Ra	+2					1.43 (A)		1.56			1.72
89	Ac	+3					1.18 (A)					
90	Th	+4					1.08		1.12	1.17		
91	Pa	+3					1.13 (A)					
		+4					0.98 (A)		1.09			
		+5					0.89 (A)		0.99	1.03		
92	U	+3					1.12					
		+4					0.97 (A)	1.06	1.08	1.13		
		+5					0.84	1.04				
		+6	0.53		0.56		0.81	0.96				
93	Np	+2					1.18					
		+3					1.10					
		+4					0.95 (A)		1.06			
94	Pu	+3					1.09					
		+4					0.88		1.04			

^aLow spin and high spin are indicated by L and H, respectively.

^bA = Ahrens (1952); P = Pauling (1927).

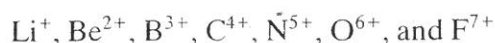
^cPb²⁺, coordination number II, radius = 1.47 Å.

SOURCE: Whittaker and Muntus (1970).

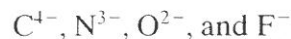
depending on the coordination number on the lattice site. Evidently, ions are not actually hard spheres, although they are treated this way in some aspects of crystal chemistry.

The ionic radii listed in Table 7.3 vary in regular patterns depending on the atomic number of the element and the charge of the ion as shown in Figure 7.5, provided all radii are based on the same coordination number. We take note first of the existence of *isoelectronic series* consisting of sequences of ions in which the charge increases with increasing atomic number and which therefore contain the same number of electrons. Such isoelectronic series exist in all

but the first period. For example, in the second period we find:

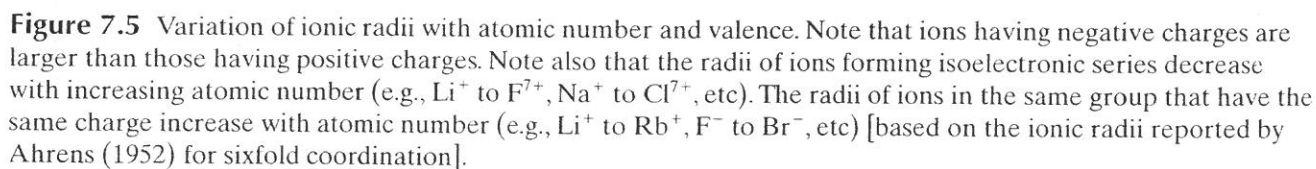


Each of these ions has only two electrons. Similarly, the ions:



form an isoelectronic series in which each ion contains 10 electrons. Other isoelectronic series in periods 3, 4, and 5 are indicated in Figure 7.5.

We will find it helpful later to have a mental image of the ionic radii and to recall some gener-



1. The ionic radii of isoelectronic series *decrease* with increasing atomic number for both positively and negatively charged ions.
2. The radii of ions with the same charge in a group *increase* with increasing atomic number, that is, downward in the periodic table.

3. The radii of ions of the same element *decrease* with increasing positive charge and *increase* with increasing negative charge.
4. The radii of ions with charges of +2 and +3 among the transition metals of the fourth period *decrease* with increasing atomic number, thereby implying a contraction of the electron cloud as the 3d orbitals are filled.
5. Ions of different elements may have similar ionic radii.

Examples to illustrate the last observation can be found in Figure 7.5 or by consulting Table 7.3.

Na ⁺ , Ca ²⁺ , Cd ²⁺ , Y ³⁺ , Ti ³⁺ , REE(+3), Th ⁴⁺	~ 1.00 Å (sixfold coordination)
Hf ⁴⁺ , Zr ⁴⁺	~ 0.80 Å (sixfold coordination)
Fe ³⁺ , Co ³⁺ , Ni ³⁺	~ 0.65 Å (sixfold coordination)

The similarity of the ionic radii of different elements is an important phenomenon because it may permit the ion of one element to substitute for an ion of another element in ionic crystals (Goldschmidt et al., 1926).

The radii of ions in aqueous solution may be significantly changed by hydration. In this connection it is helpful to define the *ionic potential* as the ratio of the charge of an ion in electronic charges to its radius measured in angstrom units. The ionic potential is a measure of the density of the electrical charge on the surface of an ion and reflects the strength of the electrostatic bond the ion can form with another ion of the opposite charge or with a polar molecule like water. Ions with high ionic potential attract more water molecules and form hydrated ions that are larger than those of ions having lower ionic potentials. For example, the radii of the hydrated ions of the alkali metals decrease from Li⁺ to Cs⁺ even though their ionic radii in crystals increase with atomic number (Table 7.3). This can be explained by considering the ionic potentials of the alkali metals: Li⁺ = 1.2, Na⁺ = 0.91, K⁺ = 0.68, Rb⁺ = 0.64, and Cs⁺ = 0.56. Therefore, even though Li⁺ (radius = 0.82 Å) is much smaller than Cs⁺ (radius = 1.78 Å), it forms a *larger* hydrated ion than Cs⁺ because of its higher ionic potential.

7.6 Summary

The chemical elements can be divided into electron donors and electron acceptors, depending on whether their valence orbitals are nearly empty or nearly full. The tendencies of elements to be electron donors, and therefore to act like metals, is reflected by their first ionization potentials and electronegativities. Elements with low ionization potentials and low electronegativities have strongly developed metallic character. In general, the metallic character of the elements decreases from left to right across the periodic table and increases downward in those groups in which the elements have valence electrons in *s*- and *p*-orbitals.

Chemical bonds can be classified into ionic or covalent bonds, depending on whether the valence electrons are effectively transferred or shared, respectively. In reality, all ionic bonds have varying degrees of covalent character as indicated by the magnitude of their electronegativity *difference*. Polar solvents such as water are able to break ionic bonds because of electrostatic interactions between ions in the solid phase and charges on the water molecules. The hydration of cations and anions further enhances the solubility of ionic solids in water.

The radius ratio of a cation with respect to the surrounding anions determines its coordination number and hence affects the three-dimensional patterns the ions form in ionic crystals. The ionic radii of the elements in the periodic table vary predictably, depending on the atomic numbers of the elements, the electrical charges of the ions, and on the coordination number.

The metallic character of the elements, the kinds of bonds they form with each other, and the radii of ions are all related to their position in the periodic table and thus to their electronic configurations.

Problems

1. Determine the percent ionic character of the following bonds, based on the electronegativity differences: (a) NaCl; (b) FeCl₂; (c) CuCl; (d) AlCl₃; (e) CCl₄.

2. Look up the ionization potentials of silicon in a recent edition of the *CRC Handbook of Chemistry and Physics* (Weast et al., 1986) and plot them in coordi-

nates of electron volts (eV) versus the number of electrons removed.

3. Explain why the third and fifth ionization potentials of silicon are significantly higher than those that immediately precede them.
4. Explain why the first ionization potential of sulfur ($Z = 16$) is less than that of phosphorus ($Z = 15$).
5. Write an equation to represent the dissociation of $(\text{NH}_4)_2\text{SO}_4$ into ions in an aqueous solution.
6. Calculate the volume of an ion of Na^+ in cubic meters (assume sixfold coordination).
7. Calculate the radius ratio for a planar structure with fourfold coordination.
8. Determine the ionic potentials of the ions in the isoelectronic series K^+ to Mn^{7+} and derive a conclusion about the size of the hydrated ions in the isoelectronic series (use sixfold and fourfold coordination depending on the availability of data in Table 7.3).

References

- AHRENS, L. H., 1952. The use of ionization potentials Part 1. Ionic radii of the elements. *Geochim. Cosmochim. Acta*, **2**:155.
- COTTON, F. A., and G. WILKINSON, 1962. *Advanced Inorganic Chemistry*. Wiley, New York, 959 pp.
- FYFE, W. S., 1964. *Geochemistry of Solids*. McGraw-Hill, New York, 199 pp.
- GOLDSCHMIDT, V. M., T. BARTH, G. LUNDE, and W. ZACHARIASEN, 1926. Geochemische Verteilungsgesetze der Elemente. VII. *Skrifter Norske Videnskaps.-Akad. Oslo, I. Mat.-Naturv. Klasse*, No. 2.
- GREENWOOD, N. N., and A. EARNSHAW, 1984. *Chemistry of the Elements*. Pergamon Press, Oxford, England, 1542 pp.
- HEYDEMANN, A., 1969. Tables. In K. H. Wedepohl (Ed.), *Handbook of Geochemistry*, vol. 1, 376–412. Springer-Verlag, Berlin, 442 pp.
- PAULING, L., 1927. The sizes of ions and the structure of ionic crystals. *J. Amer. Chem. Soc.*, **49**:763.
- PAULING, L., 1960. *Nature of the Chemical Bond*, 3rd ed. Cornell University Press, Ithaca, NY.
- SARGENT-WELCH SCIENTIFIC CO., 1980. *Periodic Table of the Elements*. 7300 Linder Ave., Skokie, IL 60076.
- SHANNON, R. D., and C. T. PREWITT, 1969. Effective crystal radii in oxides and fluorides. *Acta Crystallogr., Sect. B*, **25**:925–946.
- SHANNON, R. D., 1976. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. Sect. A*, **32**:751–767.
- WEAST, R. C., M. J. ASTLE, and W. H. BEYER, 1986. *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton, FL.
- WHITTAKER, E. J. W., and R. MUNTUS, 1970. Ionic radii for use in geochemistry. *Geochim. Cosmochim. Acta*, **34**:945–956.

Ionic Substitutions in Crystals

One of the principal objectives of geochemistry has been to explain the distribution of chemical elements in the Earth (Chapter 1). Before this objective could be achieved, it was first necessary to determine how the elements are actually distributed by analyzing large numbers of rocks and minerals from all over the Earth. F. W. Clarke took a giant step in that direction by his own efforts as an analytical chemist and by presenting the data of geochemistry in his book, first published in 1908. In subsequent years, geochemists continued to analyze geological materials in order to determine the chemical composition of the Earth and to understand the reasons for the observed variation in chemical composition of different kinds of rocks.

This was by no means an idle exercise because the information contributed directly to the understanding of the origin of metallic and nonmetallic ore deposits. The search for ore deposits of all kinds continues to be one of the principal tasks of geologists in society. In a very real sense, geologists are still expected to know where to find "the good rocks" that are the foundation of our modern industrial society.

8.1 Goldschmidt's Rules of Substitution

An important objective of Goldschmidt's work in geochemistry was to discover the laws of distribution of the chemical elements (Goldschmidt, 1937). He and Pauling (1927) saw perhaps more clearly than their contemporaries that the internal

structure of crystals could be understood in terms of the size and charge of the ions and that an ion of one element can replace the ion of another if it is similar in size and charge. These insights are summarized by a set of generalizations known as *Goldschmidt's rules of substitution*.

1. The ions of one element can extensively replace those of another in ionic crystals if their radii differ by less than about 15%.
2. Ions whose charges differ by one unit substitute readily for one another provided electrical neutrality of the crystal is maintained. If the charges of the ions differ by more than one unit, substitution is generally slight.
3. When two different ions can occupy a particular position in a crystal lattice, the ion with the higher ionic potential forms a stronger bond with the anions surrounding the site.
4. Substitution may be limited, even when the size and charge criteria are satisfied, when the competing ions have different electronegativities and form bonds of different ionic character.

The fourth rule was actually formulated by Ringwood (1955) in order to explain discrepancies that arose from the three rules proposed by Goldschmidt. For example, Na^+ and Cu^+ have the same charge and their radii are virtually identical (Ahrens, 1952). Hence, according to Goldschmidt's rules, Cu^+ should replace Na^+ in sodium minerals

such as albite ($\text{NaAlSi}_3\text{O}_8$) or halite (NaCl). We know, of course, that this substitution does not occur. The reason is that copper forms more covalent bonds than sodium, as indicated by their electronegativities.

The occurrence of elements in minerals and rocks either as major or minor constituents depends on their abundances and chemical properties. In general, the most abundant elements form the mineral compounds within which the minor elements may be accommodated by ionic substitution, in interstitial lattice positions, in fluid inclusions, or as exsolved mineral phases. Some minor elements also occur in accessory minerals such as zircon or apatite.

The tendencies of elements to form minerals are most clearly displayed during the crystallization of a cooling magma. Therefore, Goldschmidt's rules primarily apply during this process, which was thought to "sort" the ions according to their size and charge. Those ions that do not fit into the major rock-forming minerals are said to be *incompatible* and therefore accumulate in the residual magma. Consequently, the incompatible elements are concentrated in late-stage differentiates of magmas, including aplite dikes, pegmatites, and hydrothermal veins. The elements in this category include K^+ , Rb^+ , Cs^+ , Sr^{2+} , Ba^{2+} , the rare earth elements (REE), Zr^{4+} , Hf^{4+} , Nb^{5+} , Ta^{5+} , Th^{4+} , and U^{4+} . All of these elements ultimately associate themselves with rocks composed of silicate minerals and, for that reason, are also referred to as the *large ion lithophile* (LIL) group.

Goldschmidt's rules were critically reviewed by many geochemists, including Shaw (1953) and Burns and Fyfe (1967). The rules are at best a first approximation to which there are many exceptions that arise because the replacement of one ion by another is generally site-specific, especially in complex compounds. The problem is magnified because the ionic radii, used as a criterion in Goldschmidt's rules, depend on the site where the replacement takes place. In spite of these limitations, Goldschmidt's rules still serve a useful purpose by identifying some of the major factors that must be considered in the possible replacement of ions in crystals forming in a cooling magma or from an aqueous solution.

8.2 Camouflage, Capture, and Admission

According to Goldschmidt's first rule, ions that have similar radii and equal charges replace each other extensively in ionic crystals. The extent of substitution that actually takes place depends on the concentration of the ions in the medium in which the crystals are forming, on the temperature, and on the compatibility of their bonds and coordination numbers. Crystals forming at high temperature are more tolerant of foreign ions than crystals forming at a low temperature. Therefore, the concentration of trace elements in crystals can be used to estimate the temperature of formation of certain minerals. For example, the concentration of Fe^{2+} in sphalerite (Fe, ZnS) increases with the temperature provided that enough iron was available to saturate the sphalerite (Kullerud, 1959).

The second rule applies to substitution of ions of similar size but having different charges. When the charge *difference* is greater than one, substitution is limited because of the difficulty in maintaining electrical neutrality. Charge deficiencies that result from substitution of ions of unequal charge must be compensated by a second substitution involving an ion having a different charge. This process of *coupled substitution* contributes to the diversification of chemical compositions of many minerals. An alternative to coupled substitution displayed by the clay minerals is *adsorption* of ions on the charged surfaces of small crystals.

The third rule describes the effect of the ionic potential on the relative strengths of ionic bonds of ions competing for the same site. Ions having a higher ionic potential (charge/radius ratio) form a stronger bond than their competitors and are therefore preferentially incorporated into the crystal. Similarly, competing ions with lower ionic potentials are discriminated against and are initially excluded from crystals forming from a magma. Consequently, ions with high ionic potentials are concentrated in early-formed crystals in a cooling magma, whereas those with low ionic potentials are concentrated in the residual magma and enter late-forming crystals.

According to the fourth rule, a minor ion can replace a major ion only if their electronegativities are similar. When two minor ions that are similar in size and charge compete for the same site, the one whose electronegativity is more similar to that of the major ion is preferred because the bonds are more compatible.

We see that Goldschmidt's rules of substitution provide criteria for predicting the extent to which minor elements can replace major elements in the minerals they form. As a result, we can predict how minor elements distribute themselves when minerals crystallize from a cooling magma or from a supersaturated aqueous solution. Some elements are selectively concentrated into the solid phase, whereas others remain in the liquid phase. The different ways in which the ions of minor elements are *partitioned* between the solid and liquid phases are described by the terms that form the heading of this section.

Camouflage occurs when the minor element has the same charge and a similar ionic radius as the major element it is replacing.

In this case, the minor element does not form its own minerals but is hidden in the crystals of another element. Camouflage is displayed by Zr^{4+} (0.80 Å) and Hf^{4+} (0.79 Å) because hafnium rarely forms its own minerals and is always present in the mineral zircon (ZrSiO_4). We could say that zircon crystals do not distinguish between Zr^{4+} and Hf^{4+} ions and accept both with equal ease.

Capture takes place when a minor element enters a crystal preferentially because it has a higher ionic potential than the ions of the major element.

Examples of capture occur in the formation of feldspar crystals, which may capture Ba^{2+} (1.44 Å) or Sr^{2+} (1.21 Å) in place of K^+ (1.46 Å). As a result, the concentrations of these elements in the residual magma *decrease* during the crystallization of K-feldspar. However, the replacement of the univalent K^+ ion by a divalent ion requires a coupled substitution of Al^{3+} for Si^{4+}

in order to preserve the electrical neutrality of the crystal lattice.

Admission involves the entry of a foreign ion that has a lower ionic potential than the major ion because it has either a lower charge or a larger radius, or both.

The occurrence of Rb^+ in K-feldspar and other potassium minerals is an example of admission because Rb^+ (1.57 Å) has a smaller ionic potential than K^+ (1.46 Å). Other examples are the replacement of Ca^{2+} (1.08 Å) by Sr^{2+} (1.21 Å) in calcite, and the substitution of Cl^- (1.72 Å) by Br^- (1.88 Å) in chlorides. The extent to which ions are admitted into a particular lattice site *decreases* as the difference in the radii of competing ions *increases*. For example, I^- (2.13 Å) replaces Cl^- (1.72 Å) much less than Br^- (1.88 Å) and Ba^{2+} (1.44 Å) is less abundant in calcite than Sr^{2+} (1.21 Å). Evidently, admission of foreign ions into the crystal of a major element is ultimately controlled by the size criterion expressed in Goldschmidt's first rule.

The third rule makes a statement about the relationship between the ionic potentials of cations and the strength of the bonds they form with anions. This relationship manifests itself in *some cases* in the melting temperatures of the compounds they form. For example, the Mg silicate forsterite (Mg_2SiO_4) has a higher melting temperature (1910°C) than the Fe silicate fayalite (Fe_2SiO_4), which melts at 1503°C. The two minerals form a solid solution known as the mineral olivine ($(\text{Mg, Fe})_2\text{SiO}_4$), which crystallizes from cooling magmas of basaltic composition. Early formed olivine is enriched in the forsterite (Mg) end member, whereas olivine forming at lower temperatures is enriched in the fayalite (Fe) end member. A possible explanation is that early formed olivine captures Mg^{2+} (0.67 Å) in favor of Fe^{2+} (0.74 Å) because it has a higher ionic potential (Ahrens, 1952). Similarly, the feldspar anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) has a higher melting temperature than albite ($\text{NaAlSi}_3\text{O}_8$) presumably because Ca^{2+} (1.08 Å) has a higher ionic potential than Na^+ (1.10 Å) (Ahrens, 1952). As a result, early-formed plagioclase is

Table 8.1 Classification of Silicate Minerals Based on Their Structures as Illustrated in Figure 8.1

Class	Shared corners	Silicate anion	Si/O	Examples
Neso	0	SiO_4^{4-}	1 : 4	fayalite Fe_2SiO_4
Soro	1	$\text{Si}_2\text{O}_7^{6-}$	2 : 7	akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$
Cyclo	2	SiO_3^{2-}	1 : 3	benitoite $\text{BaTiSi}_3\text{O}_9$
Ino single	2	SiO_3^{2-}	1 : 3	enstatite MgSiO_3
Ino double	$2\frac{1}{2}$	$\text{Si}_4\text{O}_{11}^{6-}$	4 : 11	anthophyllite $\text{Mg}_7(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$
Phyllo	3	$\text{Si}_2\text{O}_5^{2-}$	2 : 5	kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Tekto	4	SiO_2	1 : 2	quartz SiO_2

initially enriched in calcium relative to sodium. The ionic potential by itself, however, is *not* a reliable predictor of the melting temperatures of solid compounds and the examples presented above are more the exception than the rule (Burns and Fyfe, 1967).

8.3 Coupled Substitution: Key to the Feldspars

When the ion of a major element is replaced by a foreign ion having a different charge, the electrical neutrality of the crystal must be preserved by a complementary substitution elsewhere in the crystal lattice. This phenomenon helps to explain the chemical diversity of silicate minerals such as the feldspars, zeolites, and micas.

Silicate minerals contain a framework of *silica tetrahedra* linked together to form different kinds of structures. The silicate anion (SiO_4^{4-}) forms a tetrahedron in which the Si atom is located in the center and is bonded to the four O atoms that occupy the corners of the tetrahedron. The Si—O bonds are about 50% covalent based on the difference in their electronegativities. Each O atom at the corner of a tetrahedron has an unpaired electron in a hybridized *p*-orbital that can form ionic bonds with cations in orthosilicates, such as Mg_2SiO_4 , Fe_2SiO_4 , or Li_4SiO_4 . The silica tetrahedra can also form bonds with each other by sharing O atoms at the corners to form

rings, chains, double chains, sheets, and three-dimensional networks listed in Table 8.1 and illustrated in Figure 8.1.

The feldspars are “tekto-silicates” composed of a three-dimensional network of silica tetrahedra linked at their corners. In this arrangement, the two unpaired electrons of O atoms form bonds with different Si atoms and thereby link the tetrahedra together. When all of the O atoms are shared in this manner, each silicon atom “owns” only half of each of the four O atoms located at the corners of its tetrahedron. Therefore, in a three-dimensional network the ratio of Si to O is reduced from 1 : 4 to 1 : 2 and its formula is SiO_2 .

This framework of linked silica tetrahedra can admit a limited number of Al^{3+} ions in place of Si^{4+} . The substitution is restricted because in fourfold coordination Al^{3+} (0.47 Å) is significantly *larger* than Si^{4+} (0.34 Å) and actually violates Goldschmidt’s first rule. On the other hand, the radius ratio of Al^{3+} to O^{2-} is 0.36, which allows it to have a coordination number of 4 like Si^{4+} , whose radius ratio with O^{2-} is 0.26 (see Figure 7.4). As a result, one in four Si atoms is replaced to form the aluminosilicate anion $\text{AlSi}_3\text{O}_8^-$. This anion does not actually exist in discrete form because the lattice extends continuously in all directions. However, the formula of the aluminosilicate anion allows us to recognize that the replacement of one out of every four Si atoms by Al^{3+} causes a charge imbalance of -1

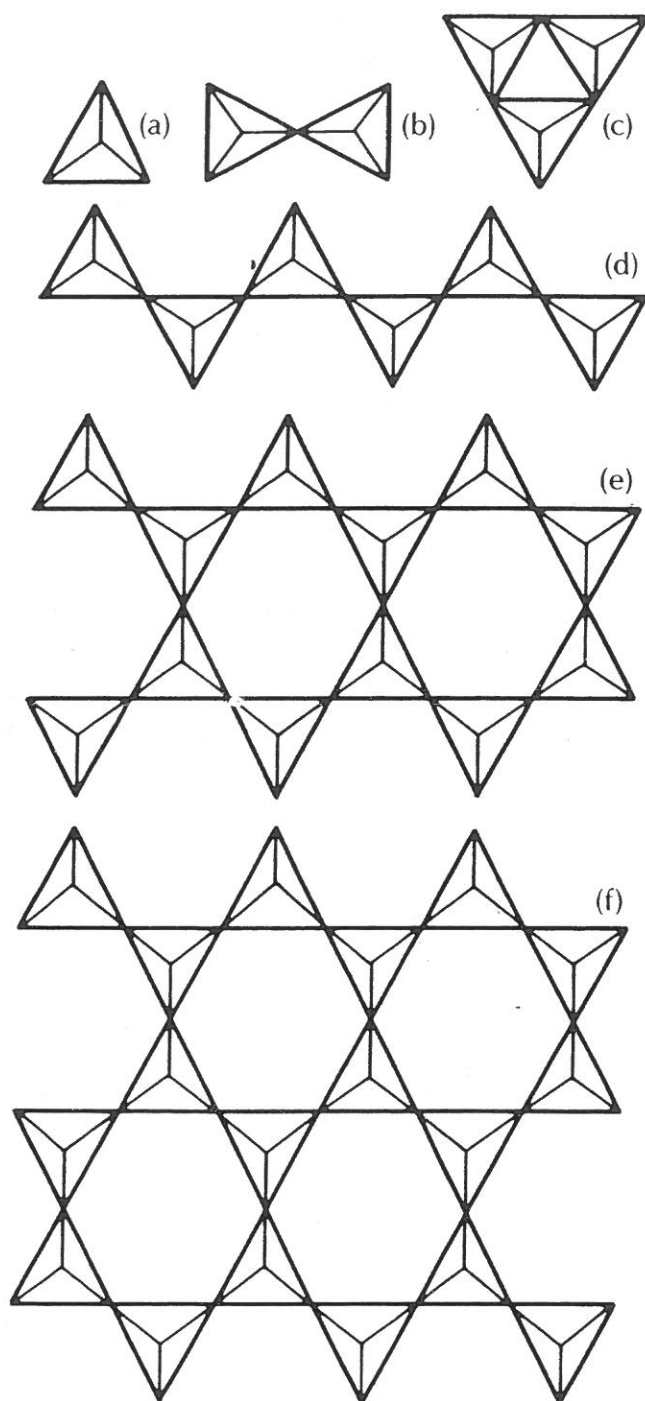


Figure 8.1 Two-dimensional networks of silica tetrahedra connected in different ways by sharing oxygen atoms at their corners. (a) Nesosilicates, (b) sorosilicates, (c) cyclosilicates, (d) inosilicates (single chain), (e) inosilicates (double chain), and (f) phyllosilicates. The tectosilicate structure, consisting of a three-dimensional network of tetrahedra in which all four oxygen atoms are shared, is not shown. More details are given in Table 8.1.

in the lattice. This excess negative charge is neutralized by the introduction of Na^+ or K^+ . The resulting compounds are known to us as the alkali feldspars:



When two out of four Si atoms are replaced by Al^{3+} , the aluminosilicate anion has a charge of -2 , which is neutralized by the addition of Ca^{2+} or Ba^{2+} to form:



Albite and anorthite form a solid solution known as plagioclase, which is subdivided into six mineral species, depending on the molar concentrations of albite (Ab) or anorthite (An).

Mineral	Ab, %	An, %
Albite	100–90	0–10
Oligoclase	90–70	10–30
Andesine	70–50	30–50
Labradorite	50–30	50–70
Bytownite	30–10	70–90
Anorthite	10–0	90–100

The series is divided into 20% increments of Ab or An, except at the ends, where the increments are 10%. The names of the plagioclase series can be remembered by noting that the first letters spell the name of the fictitious geochemist A. O. Alba.

8.4 Distribution Coefficients and Geothermometers

Goldschmidt's rules provide a rational basis for predicting how minor elements may enter crystals forming from a cooling melt or from an aqueous solution. These effects are described qualitatively as "camouflage," "capture," and "admission." However, words alone are not sufficient to describe the partitioning of minor elements

between crystals and the liquid from which they formed.

We therefore define the *distribution coefficient* (D):

$$D = \frac{C^x}{C^l} \quad (8.1)$$

where C^x is the concentration of a minor element in the crystal (x) of a mineral and C^l is the concentration of that element in the liquid (l) from which the crystal formed under equilibrium conditions. The distribution coefficient of a particular element in a specific mineral may be > 1 , < 1 , or $= 1$. The magnitude of D is related to the verbal descriptors as follows:

$$\begin{aligned} D > 1 & \quad \text{capture} \\ D < 1 & \quad \text{admission} \\ D = 1 & \quad \text{camouflage} \end{aligned}$$

The numerical values of D must be determined experimentally in the laboratory or by analysis of natural systems in which both crystals and liquid can be sampled.

The observed distribution of trace elements in crystals can be used to estimate the temperature of formation of coexisting minerals. Recall that the extent of substitution is temperature dependent because crystals become more tolerant of foreign ions as the temperature increases. Therefore, distribution coefficients are, in general, temperature dependent and are also affected by the compositions of the liquid and the crystals, as well as by pressure. If two minerals A and B coprecipitate or crystallize from the same solution or magma, a minor element (y) can enter both minerals A and B at a particular temperature. The distribution coefficients of element y are:

$$D_A = \left(\frac{C_y^x}{C_y^l} \right)_A \quad \text{and} \quad D_B = \left(\frac{C_y^x}{C_y^l} \right)_B \quad (8.2)$$

The ratio of the distribution coefficients for element y is:

$$\frac{D_A}{D_B} = \frac{(C_y^x)_A}{(C_y^x)_B} = K \quad (\text{constant}) \quad (8.3)$$

Equation 8.3 indicates that the ratio of the concentrations of the trace element y in minerals A and B is equal to a constant K , which is equal to the ratio of the distribution coefficients of y in those minerals at the temperature of formation.

In principle, the temperature dependence of the distribution coefficients of a trace element in different minerals can be determined experimentally. The temperature of formation of rock samples can then be determined from the ratio of the measured concentrations of the selected trace element in these two minerals (McIntyre, 1963).

Consider, for example, the replacement of Zn^{2+} (0.68 Å, fourfold coordination) in sphalerite (ZnS) and Pb^{2+} (1.26 Å, sixfold coordination) in galena by Cd^{2+} (0.88 Å, fourfold coordination, 1.03 Å, sixfold coordination). The electronegativities of the three elements are similar and the bonds they form with sulfur are about 85% covalent. An experimental study by Bethe and Barton (1971) indicated that Cd is strongly partitioned into sphalerite (sp) coexisting with galena (gn) between 600 and 800 °C and that the temperature dependence of the distribution coefficients is given by:

$$\log K(\text{Cd}) = \frac{(2080 - 0.0264P)}{T} - 1.08 \quad (8.4)$$

where:

$$K(\text{Cd}) = \frac{C_{sp}}{C_{gn}} \quad \text{for Cd}$$

C = concentration of CdS in weight percent

T = absolute temperature in kelvins

P = pressure in atmospheres

The relationship between $K(\text{Cd})$ and the temperature is found to be highly nonlinear when equation 8.4 is plotted in linear coordinates in Figure 8.2. However, in coordinates of $\log K$ (y -coordinate) and $1/T$ (x -coordinate) equation 8.4 is a straight line in the slope-intercept form:

$$y = mx + b \quad (8.5)$$

The slope $m = 2080 - 0.0264P$ and the intercept on the y -axis is $b = -1.08$. The pressure can be dis-

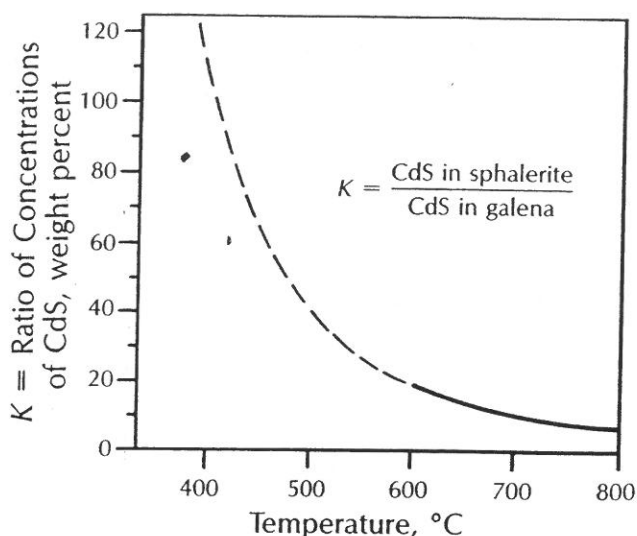


Figure 8.2 Geothermometer based on the distribution of CdS between sphalerite and galena (equation 8.4). The constant K is the ratio of the concentrations of CdS in sphalerite and galena in weight percent. The curve implies that the Cd content of sphalerite decreases relative to that of galena with increasing temperature of formation of these minerals. The solid part of the line is based on the experimental data of Bethke and Barton (1971). The dashed line is an extrapolation of those data.

regarded for low values of P . Other geothermometers studied by Bethke and Barton (1971) are based on the distributions of Mn (600–800°C) and Se (390–595°C) between sphalerite, galena, and chalcopryrite. The results indicate that Mn^{2+} , like Cd^{2+} , is preferentially incorporated into sphalerite rather than galena, whereas the order of preference for Se^{2-} is galena, chalcopryrite, and sphalerite, listed in order of decreasing preference.

The applicability of these trace element geothermometers is limited by the requirement that the minerals must have formed at the same temperature from the same solution under equilibrium conditions and that interfering effects caused by the presence of other ions or pressure variations were either negligible or cancel. These are serious limitations because minerals generally precipitate sequentially rather than simultaneously, which means that coexisting minerals do not necessarily form at the same temperature or from the same solution.

8.5 Geochemical Classification of the Elements

The geochemical classification of the elements is based on the way in which the elements actually distribute themselves between different kinds of liquids and a gas phase. During the smelting of oxide and sulfide ores three different liquids are encountered that are immiscible in each other and that segregate into layers depending on their density. These liquids are composed of molten Fe, molten sulfides (matte), and molten silicates (slag). Goldschmidt and his contemporaries considered it likely that the Earth was initially completely molten and that these liquids separated from each other under the influence of gravity to form an Fe core, a sulfide layer, and a silicate layer in the interior of the Earth. The gases formed the atmosphere, which subsequently produced the hydrosphere by condensation of water vapor.

The heat required for melting was provided by the impacts of the “planetesimals,” by compression caused by the gravitational contraction of the Earth, by the migration of dense phases toward the center of the Earth, and by the decay of the radioactive isotopes of U, Th, and K, which were more abundant at the time of formation of the Earth 4.5×10^9 years ago than they are today and therefore generated more heat than they do at present. Although the Earth does not actually contain a sulfide shell, Goldschmidt’s geochemical classification still conveys useful information about the tendencies of the elements to enter liquids of different composition or to be concentrated in the gas phase.

The information on which this classification is based came from the study of meteorites and from the smelting of the Kupferschiefer ore (copper slate) at Mansfeld in Germany. Meteorites are fragments of larger parent bodies that formed between the orbits of Mars and Jupiter (Mason, 1962) (see Table 3.2). Some of the parent bodies were large enough to retain sufficient heat for melting and differentiated into metallic Fe, silicate rocks, and sulfide minerals. The parent bodies were subsequently broken up by tides caused by the gravitational fields of Jupiter and Mars and by collisions among themselves. The remnants of the

parent bodies still occupy the space between Mars and Jupiter. Fragments resulting from collisions among them continue to be deflected into Earth-crossing orbits and impact on the Earth as meteorites. Goldschmidt, as well as Ida and Walter Noddack in Berlin, analyzed the metallic, sulfide, and silicate phases of many meteorites and determined from the results how the elements had been partitioned into the three immiscible liquids during the geochemical differentiation of the parent bodies of meteorites (Noddack and Noddack, 1930). The information derived from the study of meteorites was consistent with the chemical compositions of the silicate slag, Fe-Cu sulfide matte, and metallic Fe, all of which form during the smelting of ore.

The resulting classification of the elements in Table 8.2 contains four groups that Goldschmidt named *siderophile* (iron liquid), *chalcophile* (sulfide liquid), *lithophile* (silicate liquid), and *atmophile* (gas phase). Note that several elements occur in more than one group and that such secondary affinity is indicated by parentheses. In general, we see from Figure 8.3 that the elements in group VIIIB are *siderophile* together with C, Mo, Au, Ge, Sn, and P. The congeners of groups IB and IIB are joined by the elements Ga, In, Tl, Pb, As, Sb, and Bi, as well as by S, Se, and Te, to form the *chalcophile* group. The *lithophile* elements include the alkali metals (group IA), alkaline earths

(group IIA), the halogens (group VIIA), as well as B, Al, O, Si, and some of the transition metals such as Sc, Ti, V, Cr, Mn, and some of their congeners. The noble gases, H, and N make up the *atmophile* group.

There are a few surprises in this classification. For example, O is lithophile rather than atmophile, and C, as well as P, dissolves in metallic Fe in the absence of O. Thallium is a chalcophile element although it commonly substitutes for K^+ in silicate minerals. We note also that Au, Sn, and Mo are siderophile, and presumably have been carried away by metallic Fe to form the core of the Earth. The same is true for Co and Ni, which occur as sulfides in ore deposits but prefer liquid Fe when given a choice. On the other hand, Ti, Cr, and Mn, which are commonly associated with Fe in igneous rocks, are not siderophile but lithophile elements.

8.6 Summary

The ions of different elements can substitute for each other provided their radii, charges, and electronegativities are similar. In addition, they must be compatible with the lattice site in terms of their radius ratios and coordination numbers. Goldschmidt's rules provide a rational basis for understanding the distribution of trace elements but do *not* give enough emphasis to the character of the site of replacement in the crystal lattice.

Table 8.2 Geochemical Classification of the Elements^a

<i>Siderophile</i>	<i>Chalcophile</i>	<i>Lithophile</i>	<i>Atmophile</i>
Fe, Co, Ni	Cu, Zn, Ga	Li, Be, B, (C), —, O, F	H, He
Ru, Rh, Pd	Ag, Cd, In	Na, Mg, Al, Si, P, —, Cl	(C), N, (O), Ne
Os, Ir, Pt	—, Hg, Tl	K, Ca, (Ga), (Ge), —, —, Br	Ar, Kr, Rn
plus	plus	Rb, Sr, —, I	
Mo, Re, Au	(Ge), As, S	Cs, Ba, (Tl), plus	
(W), and	(Sn), Sb, Se	Sc, Ti, V, Cr, Mn, (Fe)	
C, P, Ge	Pb, Bi, Te	Y, Zr, Nb	
Sn, (As), (Pb)	and (Cr), (Fe)	La, Hf, Ta, W	
	(Mo)	REE, Th, —, U, and	
		(H)	

^aThe elements in parentheses occur primarily in another class.

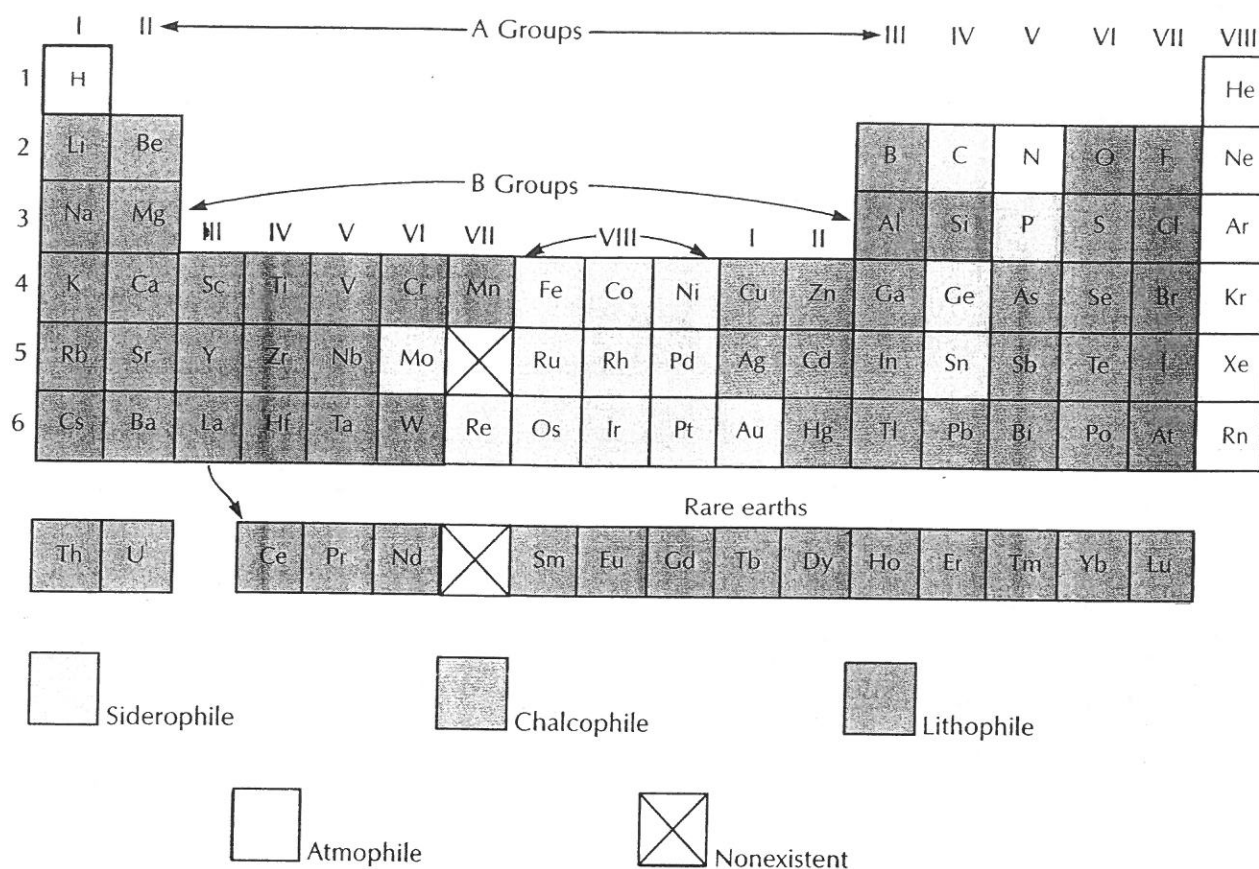


Figure 8.3 Geochemical classification of the elements in the periodic table. The classification is based on the way the elements distribute themselves between an iron liquid (siderophile), a sulfide liquid (chalcophile), a silicate liquid (lithophile), and a gas phase (atmosphile).

The extent to which replacement of ions takes place is described by the terms *camouflage*, *capture*, and *admission*. Trace elements whose ions closely resemble those of major elements in terms of size, charge, and electronegativity are *camouflaged* in the crystals formed by the major elements. Trace elements that are *captured* during the crystallization of a magma are concentrated into early-formed crystals and are depleted in the residual liquid. Ions that are *admitted* into the crystals of a major element are initially enriched in the residual magma and subsequently enter late-forming crystals.

Substitution of Al^{3+} for Si^{4+} in silicate structures causes a charge imbalance in the lattice that is neutralized by the complementary introduction of certain cations that are compatible with the particular lattice sites. This phenomenon of *coupled substitution* accounts for the chemical composi-

tion of the feldspars and of other aluminosilicate mineral groups.

The *distribution coefficient* is a quantitative measure of ionic substitution. The numerical values of distribution coefficients must be determined experimentally as a function of temperature, chemical compositions of liquids and crystals, and of pressure. The distribution of trace elements between two coexisting minerals that formed under equilibrium conditions from the same liquid can be used to determine the temperature of formation. Such geothermometers are of great interest in geochemistry but their application is restricted by the conditions that must be imposed.

The geochemical properties of the elements are reflected by their distribution between a gas phase and among natural liquids composed of

metallic Fe, transition metal sulfides, and silicates. The geochemical classification of the elements, which is based on this phenomenon, was derived

from the chemical compositions of meteorites and from metallurgical studies in the smelting of sulfide and oxide ores.

Problems

1. Determine the coordination numbers of Ca^{2+} and Sr^{2+} relative to O^{2-} , and use the result to predict the substitution of Ca^{2+} by Sr^{2+} in *calcite* (coordination : 6) and *aragonite* (coordinate : 8).

2. Predict whether Hg^{2+} can replace Sr^{2+} in the mineral *strontianite* (SrCO_3).

3. Explain the formula of *leucite* (feldspathoid, KAlSi_2O_6) in terms of coupled substitution.

4. Examine the formula of the feldspathoid *sodalite* ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$) and explain it on the basis of coupled substitution.

5. Silver (Ag^+) is a common trace element in galena where it replaces Pb^{2+} . Identify the ion of a chalcophile element that is best suited to enter galena with Ag^+ in a coupled substitution.

6. Lithium (Li^+) and Mg^{2+} have similar radii and electronegativities, yet Li^+ does not replace Mg^{2+} in olivine. Explain the reason for this occurrence and suggest another host mineral for Li^+ in which it does replace Mg^{2+} .

7. Zircon crystals (ZrSiO_4) commonly admit uranium (U^{4+}) but strongly exclude Pb. Deduce the valence of Pb in magma from this observation.

8. The melting temperatures of the fluorides of the alkali metals and alkaline earths are listed below. Consider the observed variation in terms of both the ionic character of the bonds and the ionic potentials. How should the melting temperatures vary according to Goldschmidt's rules? Which compounds conform to this prediction and which do not?

Compound	Melting temperature °C
LiF	845
NaF	993
KF	858
RbF	795
CsF	682
BeF_2	800 (sublimes)
MgF_2	1261
CaF_2	1423
SrF_2	1573
BaF_2	1355

References

- AHRENS, L. H., 1952. The use of ionization potentials Part I. Ionic radii of the elements. *Geochim. Cosmochim. Acta*, **2**:155.
- BETHKE, P. M., and P. B. BARTON, JR., 1971. Distribution of some minor elements between coexisting sulfide minerals. *Econ. Geol.*, **66**:140-163.
- BURNS, R. G., and W. S. FYFE, 1967. Trace element distribution rules and their significance. *Chem. Geol.*, **2**:89-104.
- GOLDSCHMIDT, V. M., 1937. The principles of distribution of chemical elements in minerals and rocks. *J. Chem. Soc. London*, **1937**:655-673.
- KULLERUD, G., 1959. Sulfide systems as geological thermometers. In P. H. ABELSON (Ed.), *Researches in Geochemistry*, vol. 1, 301-335. Wiley, New York, 511 pp.
- MASON, B., 1962. *Meteorites*. Wiley, New York, 274 pp.
- MCINTYRE, W. L., 1963. Trace element partition coefficients—a review of theory and applications to geology. *Geochim. Cosmochim. Acta*, **27**:1209-1264.
- NODDACK, I., and W. NODDACK, 1930. Die Häufigkeit der chemischen Elemente. *Naturwissenschaften*, **18**:757-764.
- PAULING, L., 1927. The sizes of ions and the structure of ionic crystals. *J. Amer. Chem. Soc.*, **49**:765-790.
- RINGWOOD, A. E., 1955. The principles governing trace element distribution during magmatic crystallization. *Geochim. Cosmochim. Acta*, **7**:189-202.
- SHAW, D. M., 1953. The camouflage principle and trace element distribution in magmatic minerals. *J. Geol.*, **61**:142-151.



AQUEOUS GEOCHEMISTRY AND THE STABILITY OF MINERALS

Important chemical reactions occur at the surface of the Earth when minerals are exposed to water, carbon dioxide, and oxygen. The principles that govern such reactions can be used to explain the interactions of ions in aqueous solutions and to constrain the stabilities of solid compounds with which the ions are in equilibrium. The information derivable from such studies is conveniently presented in graphical form because Earth Scientists are accustomed to using maps and diagrams in their work.

Acids and Bases

Chemical reactions in nature commonly take place in the presence of water, which acts as the medium within which ions and molecules can interact. When two ions or molecules approach each other closely, they have an opportunity to establish a bond between them. When they do so, we say that a *chemical reaction* has taken place and a product has formed. Such chemical reactions are represented by means of algebraic equations that express the balance of masses and charges of the reactants and products. We use such equations to understand chemical reactions in nature, and therefore need to develop the skill of writing and interpreting them. For this reason, we begin the third part of this book with a very simple exercise.

9.1 Chemical Reactions and Equilibria

In order to understand how chemical reactions work we first consider what happens when sodium chloride is dissolved in pure water at room temperature and atmospheric pressure. The apparatus consists of a beaker containing continuously stirred water, into which is placed an ion-sensitive electrode capable of measuring the concentration of Na^+ ions. The electrode is connected to a strip-chart recorder operating at a known chart speed. We ignore all practical limitations and complications and concentrate our attention entirely on the events that occur when we place a quantity of solid NaCl into the water in the beaker. The results of this experiment are entirely predictable based on past experience: the salt will dissolve in the water.

However, we deliberately added a *larger* quantity of salt to the beaker than will dissolve in the water it contains.

As soon as the solid NaCl comes in contact with the water in the beaker, it begins to dissolve and the concentration of Na^+ in the water increases with time. After a few minutes the Na^+ concentration becomes constant regardless of how long we continue the experiment. At this time the beaker still contains some solid NaCl that did not dissolve in the water. In order to interpret the results of this experiment we turn to Figure 9.1, which is the recorder trace of our experiment.

We see that the Na^+ concentration increased rapidly at first but eventually leveled out and became constant. When no more NaCl would dissolve in the water at the temperature and pressure of the experiment, the solution became *saturated* with respect to NaCl . When we reached that condition, the reaction achieved a state of *equilibrium* in which the rate of solution of NaCl is equal to the rate at which it precipitates. Therefore, at equilibrium the amount of excess solid NaCl and the concentrations of Na^+ and Cl^- ions in the saturated solution are *invariant* with respect to time. Once the reaction reaches equilibrium, it stops being productive because the forward and backward reactions are occurring simultaneously and at the same rates. We can indicate this condition by means of equations. At *equilibrium* the forward reaction:



and the backward reaction:



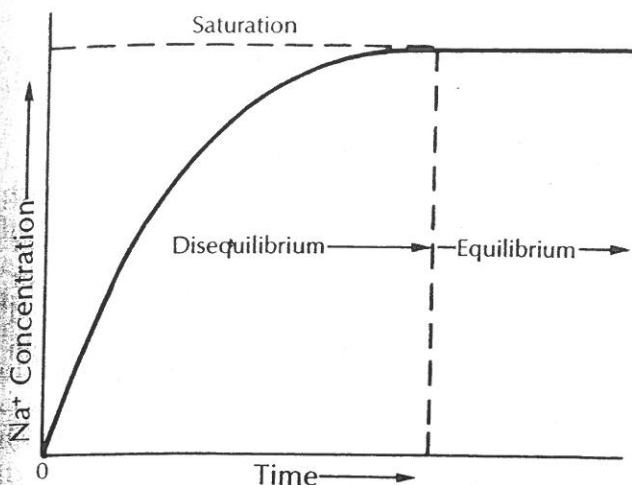
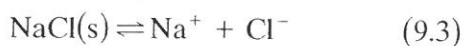


Figure 9.1 Increase of the concentration of Na^+ with time after the addition of solid NaCl to pure water at 25°C . This experiment illustrates the point that chemical reactions progress toward a state of equilibrium in which the concentrations of reactants and products are invariant with time. In this illustration the reaction reaches equilibrium when the solution becomes saturated with respect to NaCl . While reactions are at disequilibrium they effectively convert reactants into products. When reactions reach equilibrium, the rate at which products are converted back to reactants equals the forward reaction rate and, as a result, the net change in the concentrations of reactants and products is zero.

occur at the same rates. We represent this state by means of double arrows:



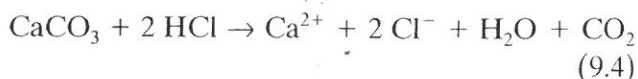
That is, double arrows mean that the reaction expressed by an equation is in a state of equilibrium.

Our experiment illustrates the important point that chemical reactions have a natural tendency to progress toward equilibrium. In order to reach this condition the reactants are consumed and products are formed such that the amounts of *both* change with time. We can think of this *disequilibrium condition* as the *active mode* of a reaction. After a reaction has reached equilibrium it becomes *inactive* in the sense that the amounts of reactants and products per unit weight or unit volume of water become constant. In fact, when a chemical reaction at equilibrium is disturbed by

changes in the physical and chemical conditions, it responds by reestablishing a new state of equilibrium. This property of chemical reactions was expressed by *Henry Le Châtelier* in 1888 in these words: Any change in one of the variables that determine the state of a system in equilibrium causes a shift in the position of equilibrium in a direction that tends to counteract the change in the variable under consideration (Moore, 1955, pp. 79–80). In other words, when a reaction at equilibrium is disturbed, it reestablishes equilibrium by counteracting the disturbance. This is the essence of *Le Châtelier's principle*. This principle will be very useful in the interpretation of equations representing chemical reactions.

Our experiment leads us also to understand the meaning of the concept of *solubility*, which is defined as the amount of a compound that dissolves to form a *saturated* solution. Therefore, in order to measure or calculate the solubility of a compound the reaction by which it dissolves must be at equilibrium. This is an important point to which we will return when we discuss solubility calculations.

The reaction we used in our experiment involves the dissociation of a solid into ions. Therefore, in this reaction no chemical bonds are actually formed by close encounters between ions or molecules. We chose that reaction mainly because it is familiar to all of us. Another reaction that is familiar to geologists is the decomposition of calcium carbonate by hydrochloric acid. This reaction can be represented by the following equation:



The carbon dioxide that is produced escapes in the form of bubbles when the reaction is carried out in contact with the atmosphere. Under these conditions the reaction cannot reach equilibrium because the CO_2 does not accumulate. Therefore, the reaction will continue in the direction indicated by the arrow in equation 9.4 until either the HCl or the CaCO_3 is used up. In this case, the reaction is prevented from reaching equilibrium and instead runs *to completion*.

Here we encounter the first of many differences between geochemistry and chemistry. In the chemistry laboratory the dissolution of CaCO_3 by HCl can be carried out in such a way that the CO_2 cannot escape. In this case, the reaction will achieve equilibrium and excess CaCO_3 and HCl will then coexist without appearing to react with each other. However, when this reaction occurs under natural conditions, it does not achieve equilibrium because the CO_2 escapes into the atmosphere. Similarly, chemical reactions on the surface of the Earth may not achieve equilibrium because some of the products continually escape either because they are gases or because ions and molecules are carried away by the movement of groundwater.

Another reason why some reactions in nature fail to achieve equilibrium is that their reaction rates are *slow*. This is especially true of reactions involving the transformation of a solid compound into another solid. Such reactions require a complex chain of events and their rates are determined by the slowest or the *rate-determining* step in the process. However, we will see that the failure of some reactions in nature to achieve equilibrium does not diminish the importance of this condition as an aid to understanding the geochemistry of the surface of the Earth.

9.2 The Law of Mass Action

The alchemists originally believed that chemical reactions occur because certain elements and compounds *love* each other. Robert Boyle expressed reservations about this idea in 1661 and Claude Louis de Berthollet pointed out about 150 years later that the direction of chemical reactions can be reversed by adding excess amounts of one of the products (Moore, 1955). The apparent reversibility of chemical reactions ultimately led to the conclusion that reactions achieve a state of equilibrium when the rate of forward reaction is equal to the rate of the backward reaction. For a simple reaction such as:



The rate of the forward reaction is:

$$v_f = k_f(\text{A})(\text{B}) \quad (9.6)$$

and the rate of the backward reaction is:

$$v_b = k_b(\text{C})(\text{D}) \quad (9.7)$$

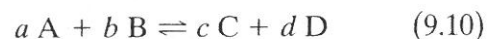
where (A), (B), (C), and (D) are the molar amounts or concentrations of the compounds or elements symbolized by A, B, C, and D and k_f and k_b are proportionality constants. At equilibrium $v_f = v_b$. Therefore:

$$k_f(\text{A})(\text{B}) = k_b(\text{C})(\text{D}) \quad (9.8)$$

which can be rewritten as:

$$\frac{k_f}{k_b} = \frac{(\text{C})(\text{D})}{(\text{A})(\text{B})} = K \quad (9.9)$$

where K is the *equilibrium constant*. In the general case of a reaction at equilibrium represented by:



the *Law of Mass Action*, first formulated by Guldberg and Waage in 1863, takes the form:

$$\frac{(\text{C})^c(\text{D})^d}{(\text{A})^a(\text{B})^b} = K \quad (9.11)$$

where a , b , c , and d are the molar coefficients taken from a balanced equation representing the reaction, and (A), (B), (C), and (D) are the concentrations of reactants and products of the reaction *at equilibrium*. The left side of equation 9.11 is the *reaction quotient*, which changes continuously as a reaction proceeds toward equilibrium. When a reaction has *achieved equilibrium*, the concentrations of reactants and products do not change and the reaction quotient becomes a *constant* known as the equilibrium constant K (Moore, 1955).

Although it is true that at equilibrium the rate of the forward reaction is equal to that of the backward reaction, the Law of Mass Action expressed in equation 9.11 cannot be derived from kinetics. The reason is that chemical reactions consist of sequences of discrete steps occurring at their own rates. Therefore, the overall rate of a

reaction is not necessarily a linear function of the molar concentrations of reactants and products, but may vary as the square, the cube, or even the square root of the concentrations. Therefore, the Law of Mass Action was initially stated only as a generalization of experimental results and did not have the force of a scientific law. It turns out, however, that the Law of Mass Action can be derived from the first and second laws of thermodynamics for reactions among ideal gases at equilibrium. In order to apply it to reactions among ions and molecules in aqueous solutions we must replace their molar concentrations by their *activities*. The activity a of an ion in solution is related to its molar concentration c by the *activity coefficient* γ such that:

$$a = \gamma c \quad (9.12)$$

The activity coefficients correct the molar concentration of ions for the interference by other ions in *real* solutions. In most cases, the values of activity coefficients are *less than one*, which indicates that the *effective concentration* (or activity) of ions is *less* than their actual concentration. Numerical values of activity coefficients can be calculated from the Debye-Hückel theory and its extensions, which we will discuss later.

The Law of Mass Action stated in equation 9.11 must now be restated in terms of activities: If a reaction represented by equation 9.10 is at equilibrium, then:

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = K \quad (9.13)$$

where the brackets [] symbolize *activities*, whereas parentheses () symbolize concentrations of ions and molecules. Unfortunately, there is no uniform convention to represent activities. We use brackets for activities and parentheses for concentrations following the example of Garrels and Christ (1965) and Krauskopf (1979), whereas Stumm and Morgan (1970) used the opposite convention and Drever (1988) symbolized activities by a lower-case a with appropriate subscripts. The difference between activity and concentration is unimpor-

tant in very *dilute* solutions and vanishes at infinite dilution when $\gamma = 1.0$. We will treat the activity coefficient as a dimensionless number, which enables us to express activities in the same units as concentration.

The units of concentration of ions and molecules in aqueous solutions are based on amounts expressed in moles but differ in terms of weight or volume of solvent or solution.

Molality (m) is the number of moles of solute per kg of water.

Formality (F) is the number of moles of solute per kg of solution.

Molarity (M) is the number of moles of solute per liter of solution.

Normality (N) is the number of equivalent weights of solute per liter of solution.

The molarity and normality are expressed in terms of volumes of solution, whereas molality and formality are based on weight of the solvent or solution, respectively. The latter are to be preferred because they are independent of the temperature, whereas molarity and normality vary with temperature because of the expansion of water with increasing temperature. The data in Table 9.1 indicate that the volume of 1 g of water increases from 1.000 13 mL at 0°C to 1.043 42 mL at 100°C or about 4.3%. Moreover, the specific volume of water has a minimum value of 1.000 00 mL at 3.98°C. Therefore, concentrations based on volumes must specify the temperature at which the volume was measured. On the other hand, it is more convenient to measure volumes of liquid than it is to weigh them. Therefore, both kinds of concentration units are in use.

When a chemical reaction between a solid and its ions and molecules in solution has achieved equilibrium, the Law of Mass Action applies with the following conventions:

1. The activities of ions and molecules must be expressed in terms of moles but may be referred to a unit weight of solvent (molality), a unit of weight of solution (formality), or a unit of volume of solution (molarity).

Table 9.1 Density and Specific Volume of Pure Water Free of Air

$T, ^\circ\text{C}$	Density, g/mL	Volume, mL/g
0	0.99987	1.00013
3.98	1.00000	1.00000
5	0.99999	1.00001
10	0.99973	1.00027
15	0.99913	1.00087
20	0.99823	1.00177
25	0.99707	1.00293
30	0.99567	1.00434
35	0.99406	1.00597
40	0.99224	1.00782
45	0.99025	1.00984
50	0.98807	1.01207
55	0.98573	1.01447
60	0.98324	1.01704
65	0.98059	1.01979
70	0.97781	1.02269
75	0.97489	1.02575
80	0.97183	1.02898
85	0.96865	1.03236
90	0.96534	1.03590
95	0.96192	1.03958
100	0.95838	1.04342

SOURCE: Weast et al. (1986), p. F-10.

2. The activities of pure solids and of water are equal to one.
3. The concentration of gases are expressed as partial pressures in atmospheres.
4. Reactions are assumed to take place at the standard temperature (25°C) and pressure (1 atm) unless otherwise indicated.

The use of *moles* as the unit of mass is required because chemical reactions result from the interactions of individual ions or molecules whose number per mole is specified by Avogadro's number. The convention that solids and water have unit activities eliminates them from the equation of the Law of Mass Action. The activity of water may, however, be less than unity in very concentrated

solutions in which the ratio of water to solute is significantly reduced. The convention to express the partial pressures of gases in units of atmospheres is arbitrary but affects the numerical values of equilibrium constants. The temperature and pressure at equilibrium must be specified because equilibrium constants vary with temperature. The effect of pressure on equilibrium constants is negligible under Earth-surface conditions.

9.3 Dissociation of Weak Acids and Bases

Following the tradition of the Swedish chemist Svante Arrhenius, we define an acid as a compound that releases hydrogen ions when it is dissolved in water. Similarly, a base is a compound that releases hydroxyl ions in aqueous solution. These definitions are no longer accepted by chemists who now prefer Brønsted's definition that an acid is any substance that can donate a proton to another substance and a base is a substance that can accept a proton. Strictly speaking, protons or hydrogen ions (H^+) cannot exist unattached in water and interact with water molecules to form hydronium ions (H_3O^+). We adopt the Arrhenius concept of acids and bases because in geochemistry we deal only with aqueous solutions of electrolytes and we will represent protons as H^+ regardless of whether they actually occur in this form.

Some acids are said to be *strong* because they release all or most of the available hydrogen ions when they are dissolved in water, whereas *weak* acids release only a small fraction of their hydrogen ions. Bases are classified similarly by the extent to which they release hydroxyl ions (OH^-) in aqueous solutions. However, the behavior of bases is more complicated because some bases do not readily dissolve in water. For example, $\text{Mg}(\text{OH})_2$ is so insoluble in water that it occurs naturally as the mineral *brucite*. Therefore, a saturated solution of brucite has a low concentration of OH^- even though $\text{Mg}(\text{OH})_2$ is a strong base and dissociates extensively into Mg^{2+} and OH^- . Some common strong acids and bases are:

Strong acids	Strong bases
Hydrochloric acid (HCl)	hydroxides of alkali metals
Nitric acid (HNO ₃)	hydroxides of alkaline earths (except Be)
Sulfuric acid (H ₂ SO ₄)	lanthanum hydroxide (La(OH) ₃)

The common weak acids include acetic acid (CH₃COOH), carbonic acid (H₂CO₃), phosphoric acid (H₃PO₄), and silicic acid (H₄SiO₄). Among the weak bases we mention ammonium hydroxide (NH₄OH), nickel hydroxide (Ni(OH)₂), copper hydroxide (Cu(OH)₂) and the hydroxides of the REEs except La. A clear distinction must be made between the *strength* of an acid or base and its *concentration*. For example, hydrochloric acid remains a strong acid even in dilute solution because it is completely dissociated. Similarly, acetic acid remains a weak acid even in a concentrated solution because it is only partially dissociated.

Many elements form hydroxides that can release either H⁺ or OH⁻ depending on the concentration of H⁺ in the water in which they dissolve. These hydroxides are said to be *amphoteric*. Among the more than 20 elements whose hydroxides are amphoteric we find Be, Al, Si, Ti, V, Fe, Co, Zn, Ag, Au, Sn, Pb, and U.

When a weak acid such as acetic acid is dissolved in water, it dissociates into ions:



Dissociation reactions like this one reach equilibrium very quickly and are then subject to the Law of Mass Action:

$$\frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = K \quad (9.15)$$

where $K = 1.76 \times 10^{-5}$ at 25°C and 1 atm. The small value of K indicates that at equilibrium most of the acetic acid will remain in the undissociated molecular form. In order to solve equation 9.15 we now specify that 0.1 mol of the compound was dissolved in 1 L of pure water

(i.e., $\gamma = 1.0$) and that an unknown fraction x dissociated into ions. Therefore, at equilibrium:

$$[\text{CH}_3\text{COOH}] = 0.1 - x$$

$$[\text{CH}_3\text{COO}^-] = [\text{H}^+] = x$$

Substituting into equation 9.15 we obtain a quadratic equation:

$$\frac{x^2}{0.1 - x} = 1.76 \times 10^{-5} \quad (9.16)$$

This equation can be solved by putting it into the standard form:

$$ax^2 + bx + c = 0 \quad (9.17)$$

which then yields the quadratic formula:

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} \quad (9.18)$$

In our case, we find that $a = 1$, $b = 1.76 \times 10^{-5}$, and $c = -1.76 \times 10^{-6}$ and that equation 9.18 yields $x_1 = +1.32 \times 10^{-3}$ and $x_2 = -1.33 \times 10^{-3}$. We discard the negative root of the quadratic equation and conclude that at equilibrium a 0.1 molar solution of acetic acid contains:

$$[\text{H}^+] = 1.32 \times 10^{-3} \text{ mol/L}$$

$$[\text{CH}_3\text{COO}^-] = 1.32 \times 10^{-3} \text{ mol/L}$$

$$[\text{CH}_3\text{COOH}] = 0.1 - 1.32 \times 10^{-3} \approx 0.1 \text{ mol/L}$$

The degree of dissociation (D) of a 0.1 molar solution of acetic acid is:

$$D = \frac{1.32 \times 10^{-3} \times 100}{0.1} = 1.32\% \quad (9.19)$$

Evidently, acetic acid is a weak acid because only 1.32% of the molecules in solution are dissociated into ions.

The first application of the Law of Mass Action has already taught us that even simple problems can result in complicated algebraic equations that are tedious to solve. We therefore resolve to make *approximations* whenever possible in order to reduce the effort required to work through to the answer. For example, going back to equation 9.16, we note that K is a very small number, which implies that only a *small fraction* of the

acetic acid molecules will dissociate. Therefore, we assume that $x \ll 0.1$ and that $0.1 - x \approx 0.1$. Equation 9.16 now reduces to:

$$\frac{x^2}{0.1} = 1.76 \times 10^{-5} \quad (9.20)$$

from which it follows immediately that:

$$x = (1.76 \times 10^{-6})^{1/2} = 1.32 \times 10^{-3} \quad (9.21)$$

Therefore, x really is much less than 0.1 and our assumption was justified. The final result is indistinguishable from the value we obtained by solving a quadratic equation.

Another lesson we can learn here is that most numerical problems in geochemistry are based on conceptual models whose validity as representations of reality is limited. For this reason, it is inappropriate to extend numerical solutions of problems to more than two or three significant figures. Similarly, a difference of 10% between approximate and exact solutions is acceptable in many cases. In fact, approximate solutions have a special virtue because they force the investigator to develop some insight into a problem before attempting to solve it.

We have seen that acetic acid releases hydrogen ions when it is dissolved in water. However, water is itself dissociated into ions:



and the dissociation constant at 25°C is, to a very good approximation, $K_w = 1 \times 10^{-14}$. According to equation 9.22, pure water contains equal concentrations of hydrogen and hydroxyl ions whose activities are derivable from the Law of Mass Action:

$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = 1 \times 10^{-14} \quad (9.23)$$

Since $[\text{H}_2\text{O}] = 1.0$ by convention and since $[\text{H}^+] = [\text{OH}^-]$, we find that in pure water:

$$[\text{H}^+] = 1 \times 10^{-7} \text{ mol/L} \quad (9.24)$$

The activity of hydrogen ions is a useful parameter because it reflects directly or indirectly the

progress of chemical reactions that may be occurring in an aqueous solution and because it can be measured by electrical methods (Stumm and Morgan, 1970). Therefore, the activity of hydrogen ions is commonly expressed as the pH value, defined by:

$$\text{pH} = -\log_{10}[\text{H}^+] \quad (9.25)$$

It follows from equation 9.24 that the pH of pure water at 25°C is equal to 7.0. When the hydrogen ion activity of a solution is greater than 10^{-7} mol/L, its pH is less than 7, and when its activity is less than 10^{-7} mol/L, the pH is greater than 7. These statements therefore define the *pH scale* according to which $\text{pH} < 7.0$ at 25°C indicates acidic conditions and $\text{pH} > 7.0$ indicates basic conditions.

In conclusion, we can now calculate the pH of a 0.1 molar solution of acetic acid. According to equation 9.21, $[\text{H}^+] = 1.32 \times 10^{-3}$ mol/L from which we calculate the pH by applying equation 9.25:

$$\text{pH} = -\log(1.32 \times 10^{-3}) = 2.88 \quad (9.26)$$

The hydrogen ions released by the acetic acid affect the activity of hydroxyl ions that must remain in equilibrium with water. Therefore, from equation 9.23:

$$\begin{aligned} [\text{OH}^-] &= \frac{1 \times 10^{-14}}{1.32 \times 10^{-3}} \\ &= 0.757 \times 10^{-11} \text{ mol/L} \end{aligned} \quad (9.27)$$

The hydroxyl ion activity can be expressed as pOH defined by:

$$\text{pOH} = -\log_{10}[\text{OH}^-] \quad (9.28)$$

In the solution of acetic acid $\text{pOH} = -\log(0.757 \times 10^{-11}) = 11.12$. Evidently, it follows from equation 9.23 that at 25°C:

$$\text{pH} + \text{pOH} = 14.0 \quad (9.29)$$

The dissociation constant of water, like all other equilibrium constants, varies with temperature, as shown in Table 9.2. Therefore, the "neutral

Table 9.2 Dissociation Constant (K_w) of Water at Different Temperatures

$T, ^\circ\text{C}$	$-\log K_w$	$T, ^\circ\text{C}$	$-\log K_w$
0	14.9435	30	13.8330
5	14.7338	35	13.6801
10	14.5346	40	13.5348
15	14.3463	45	13.3960
20	14.1669	50	13.2617
24	14.0000	55	13.1369
25	13.9965	60	13.0171

SOURCE: Weast et al. (1986), p. D-164.

point" of the pH scale is at $\text{pH} = 7.0$ only at 25°C . Actually, the data in Table 9.2 indicate that $K_w = 10^{-14.0}$ at 24°C and at 25°C it is slightly *larger* than this value.

Several weak acids are capable of yielding two or more hydrogen ions or protons per molecule of acid. When such acids dissolve in water they dissociate stepwise such that each step has a different degree of dissociation. Many bases behave exactly the same way when they dissociate in water to form OH^- . In order to illustrate the application of the Law of Mass Action to weak diprotic acids we choose hydrosulfuric acid (H_2S). This compound is a gas that dissolves in water to form H_2S molecules in aqueous solution, represented by $\text{H}_2\text{S}(\text{aq})$, which then dissociate in two steps:



where $K_1 = 10^{-7.0}$ and $K_2 = 10^{-12.9}$ (Krauskopf, 1979). The reactions rapidly achieve equilibrium and then satisfy the Law of Mass Action:

$$\frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = 10^{-7.0} \quad (9.32)$$

$$\frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} = 10^{-12.9} \quad (9.33)$$

Here we encounter for the first time two simultaneous equilibria that have two ions in common (H^+ and HS^-). Obviously, these ions must each

have the same concentration in both of the equilibria in which they occur. However, the amount of H^+ produced by the first equilibrium (9.30) is much greater than that contributed by the second equilibrium (9.31) because K_1 is about 1 million times larger than K_2 .

The problem is to calculate the activities of all ionic and molecular species in a solution containing 0.1 mol of H_2S dissolved in 1 L of pure water at 25°C . We will demonstrate *two* strategies for solving problems involving two or more simultaneous equilibria:

1. Stepwise solution.
2. Simultaneous equations.

The stepwise method applies to the dissociation of weak acids and bases, where the dissociation constants of successive steps differ by orders of magnitude. However, the use of simultaneous equations is more exact and applies to all situations in which several reactions are involved.

The stepwise method is based on simplifying assumptions that the reactions reach equilibrium in sequence. Therefore, we turn first to reaction 9.30 and let x be the number of moles of $\text{H}_2\text{S}(\text{aq})$ that dissociate. At equilibrium we then have:

$$[\text{H}_2\text{S}(\text{aq})] = 0.1 - x$$

$$[\text{H}^+] = x$$

$$[\text{HS}^-] = x$$

From the Law of Mass Action we obtain:

$$\frac{x^2}{0.1 - x} = 10^{-7.0} \quad (9.34)$$

Since K_1 is a very small number, we predict that only a small fraction of $\text{H}_2\text{S}(\text{aq})$ will be dissociated at equilibrium, which justifies the assumption that $x \ll 0.1$ and that $0.1 - x \approx 0.1$. Therefore, equation 9.34 becomes:

$$\frac{x^2}{0.1} = 10^{-7.0} \quad (9.35)$$

from which it follows that $x = 10^{-4.0}$, $[\text{H}^+] = [\text{HS}^-] = 10^{-4.0}$ mol/L, and $\text{pH} = 4.0$. The degree of dissociation of $\text{H}_2\text{S}(\text{aq})$ is:

$$D_1 = \frac{10^{-4.0} \times 100}{0.1} = 0.1\% \quad (9.36)$$

Therefore, the assumption that $x \ll 0.1$ was justified in this case.

A certain number of HS^- molecules dissociate further to form S^{2-} and additional H^+ . We let y be the number of moles of HS^- that dissociate and set:

$$[\text{HS}^-] = 10^{-4} - y$$

$$[\text{H}^+] = 10^{-4} + y$$

$$[\text{S}^{2-}] = y$$

Then, from the equation 9.33:

$$\frac{(10^{-4} + y)(y)}{(10^{-4} - y)} = 10^{-12.9} \quad (9.37)$$

We again simplify the problem with the assumption that $y \ll 10^{-4.0}$ and that $10^{-4.0} + y \approx 10^{-4.0}$ and $10^{-4.0} - y \approx 10^{-4.0}$. It follows that equation 9.37 reduces to $y = 10^{-12.9}$, which confirms the validity of the assumption that $y \ll 10^{-4.0}$ and indicates that the degree of dissociation is:

$$D_2 = \frac{10^{-12.9} \times 100}{10^{-4.0}} = 10^{-6.9}\% \quad (9.38)$$

These calculations therefore indicate that a 0.1 molar solution of $\text{H}_2\text{S}(\text{aq})$ contains the following ions and molecules:

$$[\text{H}_2\text{S}] = 0.1 - 10^{-4.0} = 0.1 \text{ mol/L}$$

$$[\text{HS}^-] = 10^{-4.0} - 10^{-12.9} = 10^{-4.0} \text{ mol/L}$$

$$[\text{H}^+] = 10^{-4.0} + 10^{-12.9} = 10^{-4.0} \text{ mol/L}$$

$$[\text{S}^{2-}] = 10^{-12.9} \text{ mol/L}$$

The second dissociation of H_2S contributes only a negligible amount of H^+ , but it provides *all* of the S^{2-} ions whose activity is equal to the value of the second dissociation constant.

The stepwise method presented above is inexact because it treats the two simultaneous equilibria as though they were independent of each other. If we look again at equations 9.30 and 9.31, we can see that the dissociation of HS^- (equation 9.31) causes more H_2S to dissociate

(equation 9.30) in accordance with Le Châtelier's principle. However, the stepwise solution disregards this interdependence of simultaneous equilibria having common ions.

The dissociation of $\text{H}_2\text{S}(\text{aq})$ can be represented exactly by means of *simultaneous equations* derived from applications of the Law of Mass Action and from the requirement of electrical neutrality and mass balance. The number of equations required to solve the problem must be equal to the number of unknown parameters. In this case we have five unknowns: $\text{H}_2\text{S}(\text{aq})$, HS^- , S^{2-} , H^+ , and OH^- , and therefore we require five equations. The first two arise from the application of the Law of Mass Action to the two dissociation equilibria and were stated previously as equations 9.30 and 9.31. To these we add an equation based on the dissociation of water:

$$[\text{H}^+][\text{OH}^-] = 10^{-14.0} \quad (9.39)$$

Next, we recall that all sulfur species in the solution arise by dissociation of $\text{H}_2\text{S}(\text{aq})$ whose initial concentration was 0.1 mol/L. Therefore:

$$(\text{H}_2\text{S}) + (\text{HS}^-) + (\text{S}^{2-}) = 0.1 \quad (9.40)$$

Note that the mass balance equation must be stated in terms of concentrations rather than activities. However, in dilute solutions the activity coefficients of all ions are close to unity and the difference between activities and concentration therefore vanishes. The fifth equation is derived from the requirement of electrical neutrality:

$$(\text{H}^+) = 2(\text{S}^{2-}) + (\text{HS}^-) + (\text{OH}^-) \quad (9.41)$$

which states that the sum of the positive charges in the solution must be equal to the sum of the negative charges. The molar concentration of S^{2-} is multiplied by 2 because each S^{2-} ion contributes two charges. Once again we see the importance of Avogadro's law because it allows us to relate the quantity of an ion or molecule, expressed in moles, to the corresponding number of ions or molecules.

We now have five independent equations that express relationships among the five unknowns and therefore we can solve the problem. The procedure is to express the activities of the ions in terms of one of the ions, and then to substitute

these relationships (after converting them to concentrations) into the equation for electrical neutrality because that equation contains all of the ions in the solution. We then solve this equation, by trial and error if necessary, and use the result to calculate the activities of all of the other ions and molecules in the solution.

Once again, the sensible approach is to make simplifying assumptions that reduce the computational labor without compromising the validity of the results. In the case at hand, we assume that $[\text{OH}^-] \ll [\text{H}^+]$ because we are discussing the dissociation of an *acid*. Therefore, we may omit the hydroxyl ion in summations such as equation 9.41 but *not* from multiplications such as equation 9.39. In addition, we know from past experience that $[\text{S}^{2-}] \ll [\text{HS}^-]$ because $K_2 \ll K_1$. This assumption simplifies both equations 9.40 and 9.41. From equation 9.40 we obtain:

$$(\text{H}_2\text{S}) + (\text{HS}^-) = 0.1 \quad (9.42)$$

and from 9.41:

$$(\text{H}^+) = (\text{HS}^-) \quad (9.43)$$

The latter can be used to revise equations 9.32 and 9.33. From equation 9.32 we obtain:

$$\frac{[\text{HS}^-]^2}{[\text{H}_2\text{S}]} = 10^{-7.0} \quad (9.44)$$

and from equation 9.33:

$$[\text{S}^{2-}] = 10^{-12.9} \text{ mol/L} \quad (9.45)$$

Next, we use equation 9.44 to express $[\text{H}_2\text{S}]$ as $[\text{HS}^-]^2/10^{-7.0}$ and substitute this value into equation 9.42:

$$\frac{[\text{HS}^-]^2}{10^{-7.0}} + \text{HS}^- = 0.1 \quad (9.46)$$

Multiplying by $10^{-7.0}$ and rearranging terms yields:

$$[\text{HS}^-]^2 + 10^{-7.0}[\text{HS}^-] - 10^{-8.0} = 0 \quad (9.47)$$

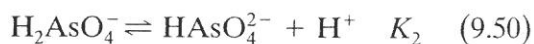
We solve this equation by means of the quadratic formula (equation 9.18) and obtain:

$$[\text{HS}^-] = \frac{-10^{-7.0} \pm [10^{-14.0} - 4(-10^{-8.0})]^{1/2}}{2} \quad (9.48)$$

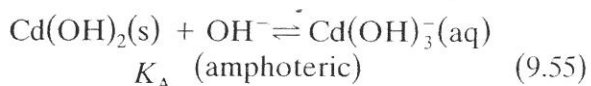
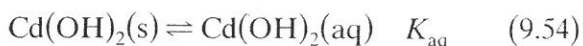
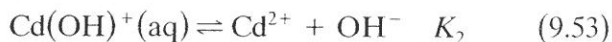
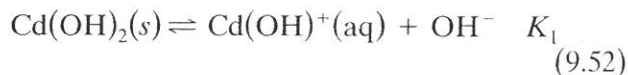
which reduces to $[\text{HS}^-] = 1 \times 10^{-4.0} \text{ mol/L}$.

Evidently, in this case, the stepwise approach yields the same results as the solution of simultaneous equations because the dissociation constants are not only small numbers but also differ from each other by a factor of nearly 1 million. These circumstances do not apply to all of the acids and bases whose dissociation constants are listed in Table 9.3. Moreover, we will encounter sets of simultaneous equilibria in which the sequential treatment is inappropriate and which can be solved only by means of a set of independent equations.

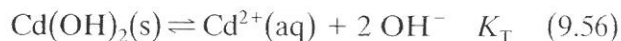
The dissociation constants listed in Table 9.3 apply *only* to specific equations. In the case of a polyprotic acid such as arsenic acid the appropriate equations are:



Note that the acid molecule H_3AsO_4 is already dissolved in water in the first dissociation step. The situation is more complicated for bases because some of them are insoluble and because they may also be amphoteric (A). We choose $\text{Cd}(\text{OH})_2$ to define the appropriate equations:



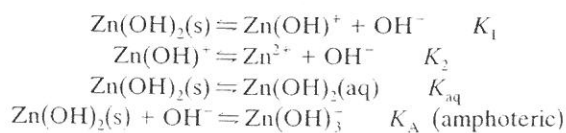
The two dissociation steps may be combined by adding equations 9.52 and 9.53. In this operation $\text{Cd}(\text{OH})^+$ cancels, and we obtain:



where $K_{\text{T}} = K_1 \times K_2$. Equation 9.54 represents the solution of solid $\text{Cd}(\text{OH})_2$ to form molecular $\text{Cd}(\text{OH})_2$ in aqueous solution. We can incorporate that step into the dissociation equilibria by

Table 9.3 Dissociation Constants of Acids and Bases at 25°C^a

Name	Formula	pK ₁	pK ₂	pK ₃	pK _A	pK _{aq}	Ref. ^b
Acids							
Acetic	CH ₃ COOH	4.75	—	—	—	—	1
Arsenious	H ₃ AsO ₃ (aq)	9.2	—	—	—	—	2
Arsenic	H ₃ AsO ₄ (aq)	2.2	7.0	11.5	—	—	2
Boric	H ₃ BO ₃ (aq)	9.2	—	—	—	—	2
Carbonic	H ₂ CO ₃ (aq)	6.35	10.3	—	—	—	2
Hydrofluoric	HF(aq)	3.2	—	—	—	—	2
Phosphoric	H ₃ PO ₄	2.1	7.2	12.4	—	—	2
Hydrosulfuric	H ₂ S(aq)	7.0	12.9?	—	—	—	2
Sulfuric	H ₂ SO ₄ (aq)	—	2.0	—	—	—	2
Hydroselenic	H ₂ Se(aq)	3.9	15.0	—	—	—	2
Selenic	H ₂ SeO ₄ (aq)	—	1.9	—	—	—	2
Silicic	H ₄ SiO ₄	9.71	13.28	9.86	13.1 (pK ₄)	—	3
Bases (Hydroxides)							
Ammonium	NH ₄ OH(aq)	4.7	—	—	—	—	2
Aluminum, amorph.	Al(OH) ₃	12.3	10.3	9.0	-1.1	—	2
Aluminum, gibbsite	Al(OH) ₃	14.8	10.3	9.0	1.4	—	2
Beryllium, amorph.	Be(OH) ₂	—	—	—	2.2	—	2
Cadmium	Cd(OH) ₂	10.5	3.9	—	4.1?	6.7	2
Cobalt	Co(OH) ₂	10.6	4.3	—	5.2	6.5	2
Copper	Cu(OH) ₂	13.0	6.3	—	2.9	—	2
Ferrous	Fe(OH) ₂	10.6	4.5	—	5.1	8.4?	2
Ferric, amorph.	Fe(OH) ₃	16.5	10.5	11.8	4.4	—	2
Lead, red	PbO + H ₂ O	9.0	6.3	—	1.4	4.4	2
Magnesium	Mg(OH) ₂	8.6	2.6	—	—	—	2
Manganese	Mn(OH) ₂	9.4	3.4	—	5.1	—	2
Mercurous, red	HgO + H ₂ O	14.8	10.6	—	4.5	3.6	2
Nickel	Ni(OH) ₂	11.1	4.1	—	4	7	2
Silver	$\frac{1}{2}$ Ag ₂ O + $\frac{1}{2}$ H ₂ O	—	—	—	3.4	5.7	2
Thorium, amorph.	Th(OH) ₄	—	—	10.3	5.8	10.8 (pK ₄)	2
UO ₂	UO ₂ (OH) ₂	14.2	8.2	—	3.6	—	2
Vanadium	V(OH) ₃	—	—	11.7	—	—	2
VO	VO(OH) ₂	15.2	8.3	—	—	—	2
Zinc, amorph.	Zn(OH) ₂	10.5	5.0	—	1.9	4.4?	2

^aExplanations: pK = -log K

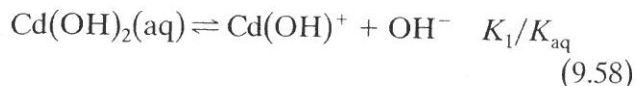
"—" means "does not apply" or "unknown".

^b(1) Weast et al. (1986); (2) Krauskopf (1979); (3) calculated from thermodynamic data of Lindsay (1979).

combining equation 9.54 and 9.52. In order to accomplish this, we first invert equation 9.54:



and we then add it to equation 9.52, thereby eliminating $\text{Cd}(\text{OH})_2(\text{s})$:



Evidently, these equations can be manipulated algebraically with the understanding that:

1. When equations are added, their equilibrium constants are multiplied.
2. When equations are subtracted, their equilibrium constants are divided.
3. When an equation is reversed, its equilibrium constant is inverted.

Finally, we note that equation 9.55 reflects the amphoteric nature of $\text{Cd}(\text{OH})_2$ because, when it takes on an additional hydroxyl ion to form $\text{Cd}(\text{OH})_3^-$, a hydrogen ion is released by the dissociation of water. Therefore, $\text{Cd}(\text{OH})_2$ in this case acts as an acid because it releases H^+ into solution. We predict, in accordance with Le Châtelier's principle, that the amphoteric character of $\text{Cd}(\text{OH})_2$ is *enhanced* in basic solutions because a high activity of OH^- causes the equilibrium to make more $\text{Cd}(\text{OH})_3^-$ in order to reduce the activity of OH^- . Conversely, in acidic solutions, which have a low activity of OH^- , the reaction shifts to the left by converting $\text{Cd}(\text{OH})_3^-$ to OH^- and $\text{Cd}(\text{OH})_2$. Therefore, amphoteric hydroxides act like acids in basic environments and like bases in acidic environments.

The behavior of amphoteric hydroxides teaches us two important lessons:

1. Weak acids and bases do *not* control the pH of natural environments but instead respond to it.
2. The solubility of sparingly soluble bases is pH dependent.

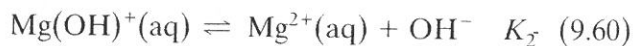
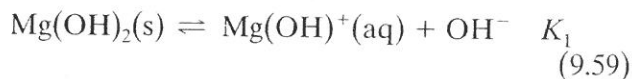
In geochemistry the pH is an *environmental parameter* that is determined by all of the simultane-

ous equilibria existing in a given environment. Therefore, the degree of dissociation of weak acids and bases and the resulting solubility of otherwise insoluble weak bases are controlled by the activity of H^+ ions in the environment.

9.4 Solubility of Sparingly Soluble Bases

We have defined the solubility of a compound as the amount of the compound that dissolves to form a saturated solution. Since many bases are only sparingly soluble, we may use the Law of Mass Action to calculate their solubilities. We choose $\text{Mg}(\text{OH})_2$ for this demonstration because it has a low solubility and therefore occurs as the mineral *brucite*.

The first and most important step toward the solution of a problem involving the Law of Mass Action is to write the equations that represent the relevant equilibria. The dissociation of $\text{Mg}(\text{OH})_2$ proceeds in two steps:



According to Table 9.3, $K_1 = 10^{-8.6}$ and $K_2 = 10^{-2.6}$. Evidently, in this case, K_2 is 1 million times *larger* than K_1 , which may cause a problem if we attempt a stepwise solution. Therefore, we decide to treat the problem by means of a set of simultaneous equations. We have four unknowns [$\text{Mg}(\text{OH})^+$, Mg^{2+} , OH^- , and H^+] and therefore need four independent equations to determine the activities of all ions in a saturated solution of brucite in pure water. We elect not to specify the pH of the solution at this time in order to demonstrate the pH dependence of the solubility of $\text{Mg}(\text{OH})_2$, but we do set all *activity coefficients* equal to *one* and thereby equate activities and concentrations.

The necessary equations are derived from the dissociation equilibria of $\text{Mg}(\text{OH})_2$ and H_2O and from the requirement of electrical neutrality:

$$[\text{Mg}(\text{OH})^+][\text{OH}^-] = 10^{-8.6} \quad (9.61)$$

$$\frac{[\text{Mg}^{2+}][\text{OH}^-]}{[\text{Mg}(\text{OH})^+]} = 10^{-2.6} \quad (9.62)$$

$$[\text{H}^+][\text{OH}^-] = 10^{-14.0} \quad (9.63)$$

$$(\text{OH}^-) = 2(\text{Mg}^{2+}) + (\text{MgOH}^+) + (\text{H}^+) \quad (9.64)$$

In order to simplify the problem, we assume that $(\text{H}^+) \ll (\text{OH}^-)$ and therefore drop (H^+) from equation 9.64. Equations 9.61 and 9.62 allow us to relate the Mg-bearing ions to $[\text{OH}^-]$:

$$[\text{Mg}(\text{OH})^+] = \frac{10^{-8.6}}{[\text{OH}^-]} \quad (9.65)$$

$$\begin{aligned} [\text{Mg}^{2+}] &= \frac{10^{-2.6}[\text{Mg}(\text{OH})^+]}{[\text{OH}^-]} \\ &= \frac{10^{-11.2}}{[\text{OH}^-]^2} \end{aligned} \quad (9.66)$$

Substituting into equation 9.64 yields:

$$[\text{OH}^-] = \frac{2 \times 10^{-11.2}}{[\text{OH}^-]^2} + \frac{10^{-8.6}}{[\text{OH}^-]} \quad (9.67)$$

After multiplying by $[\text{OH}^-]^2$ and rearranging terms, we obtain one equation in one unknown:

$$\begin{aligned} [\text{OH}^-]^3 - 10^{-8.6}[\text{OH}^-] &= 2 \times 10^{-11.2} \\ &= 1.26 \times 10^{-11} \end{aligned} \quad (9.68)$$

The equation can be solved by trial and error. We assume that $[\text{OH}^-] > 10^{-7}$ because $\text{Mg}(\text{OH})_2$ is a base. When we try $[\text{OH}^-] = 10^{-4.0}$ in equation 9.68, we obtain:

$$10^{-12.0} - 10^{-12.6} = 7.5 \times 10^{-13} \quad (9.69)$$

which is less than 1.26×10^{-11} . Further trials indicate that equation 9.68 is solved satisfactorily when $[\text{OH}^-] = 10^{-3.63}$ mol/L. Therefore, the activities of the Mg-bearing ions from the equations 9.65 and 9.66 are:

$$\begin{aligned} [\text{Mg}(\text{OH})^+] &= \frac{10^{-8.6}}{10^{-3.63}} = 10^{-4.97} \\ &= 1.07 \times 10^{-5} \text{ mol/L} \end{aligned} \quad (9.70)$$

$$\begin{aligned} [\text{Mg}^{2+}] &= \frac{10^{-11.2}}{10^{-7.26}} = 10^{-3.94} \\ &= 11.48 \times 10^{-5} \text{ mol/L} \end{aligned} \quad (9.71)$$

The solubility of $\text{Mg}(\text{OH})_2$ in pure water at 25°C is the *sum* of the concentrations of the two Mg-bearing ions and therefore equals 12.55×10^{-5} mol/L. Since the molecular weight of $\text{Mg}(\text{OH})_2$ is 58.3267, we can express its solubility as $58.3267 \times 12.55 \times 10^{-5} = 7.32 \times 10^{-3}$ g/L, which is not a large amount. The activity of H^+ in a saturated solution of $\text{Mg}(\text{OH})_2$ in pure water is $10^{-14.0}/10^{-3.63} = 10^{-10.37}$ mol/L and the pH = 10.37. Evidently a saturated solution of $\text{Mg}(\text{OH})_2$ is strongly basic.

The relationship between the activities of the Mg ions in a saturated solution of $\text{Mg}(\text{OH})_2$ and the pH is indicated by equations 9.65 and 9.66. By taking logarithms and converting pOH to pH by means of equation 9.69, we obtain from equation 9.65:

$$\log [\text{Mg}(\text{OH})^+] = -8.6 + \text{pOH} \quad (9.72)$$

or

$$\log [\text{Mg}(\text{OH})^+] = 5.4 - \text{pH} \quad (9.73)$$

Similarly, from equation 9.66:

$$\log [\text{Mg}^{2+}] = 16.8 - 2\text{pH} \quad (9.74)$$

Each of these equations has been plotted in Figure 9.2 in coordinates of the log of the activity and pH. The total solubility of $\text{Mg}(\text{OH})_2$ is the sum of the concentrations of $\text{Mg}(\text{OH})^+$ and Mg^{2+} at different values of the pH.

Equations 9.73 and 9.74 are straight lines that intersect at pH = 11.4. We see by inspection of Figure 9.2 that Mg^{2+} is the dominant ion at pH values < 11.4, whereas $\text{Mg}(\text{OH})^+$ becomes dominant in more basic solutions. Such extremely basic environments occur only in highly saline lakes such as Lake Natron in East Africa. Therefore, Mg^{2+} is the dominant ion in most geological environments. Brucite is very soluble in acidic solutions and can occur in contact with water only when the activity of Mg^{2+} is large

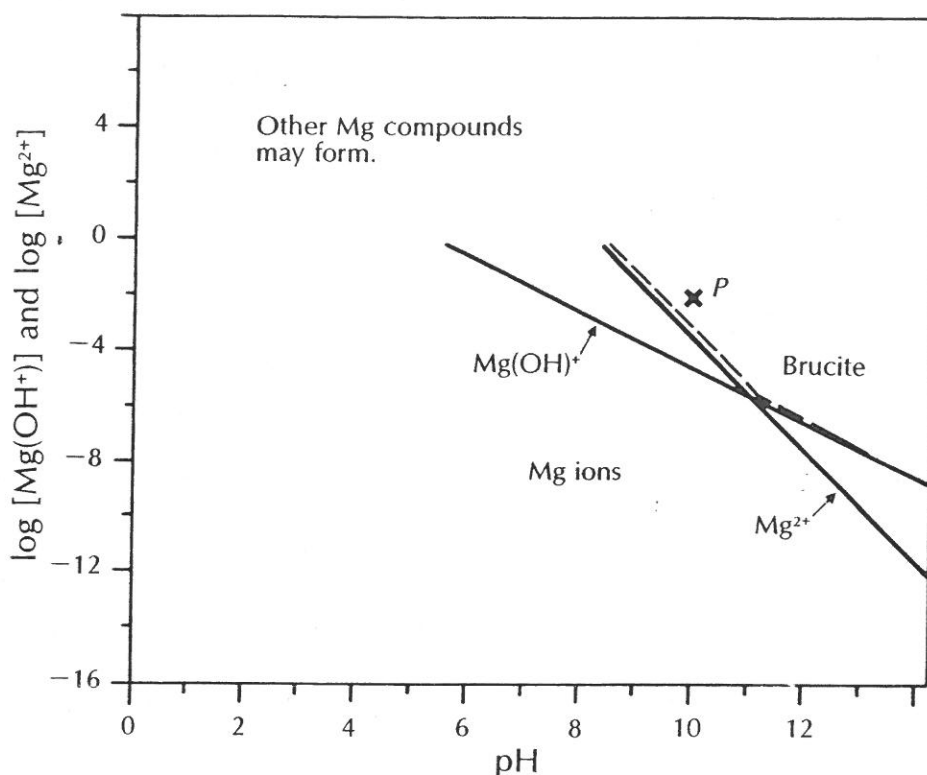


Figure 9.2 Solubility of brucite ($\text{Mg}(\text{OH})_2$) in pure water at 25°C as a function of pH. $\text{Mg}(\text{OH})_2$ dissociates to form $\text{Mg}(\text{OH})^+$ and Mg^{2+} ions, whose activities in a saturated solution are strongly pH dependent, as given by equations 9.73 and 9.74. The resulting solubility of brucite is the sum of the concentrations of the Mg-bearing ions in the solution and is indicated by the dashed line. The coordinates of point P on the diagram represent conditions that will cause brucite to precipitate. The straight lines representing activities of Mg^{2+} and $\text{Mg}(\text{OH})^+$ have been arbitrarily terminated at unit activities because in nature other Mg compounds will precipitate at elevated concentrations of Mg ions.

enough to maintain equilibrium. Therefore, the solubility of brucite in water can be used to define its stability as a solid phase in a geological environment.

Consider point P in Figure 9.2 whose coordinates are $[\text{Mg}^{2+}] = 10^{-2} \text{ mol/L}$ and $\text{pH} = 10$. The coordinates of P do not satisfy equation 9.74, which implies that brucite cannot be in equilibrium with a solution of that composition because, at this value of $[\text{Mg}^{2+}]$, the activity of OH^- is too high. The application of Le-Chatelier's principle to equations 9.59 and 9.60 indicates that the presence of excess OH^- will result in the precipitation of solid $\text{Mg}(\text{OH})_2$ until both $[\text{Mg}^{2+}]$ and $[\text{OH}^-]$ have been reduced sufficiently to place point P on

the equilibrium line. We conclude, therefore, that brucite will precipitate in all environments that lie to the right of the solubility limits in Figure 9.2. In other words, the activities of the ions formed by $\text{Mg}(\text{OH})_2$ constrain its stability in contact with water containing Mg^{2+} and $\text{Mg}(\text{OH})^+$.

9.5 pH Control of Dissociation Equilibria

The dissociation of weak acids and bases is controlled by the pH of the geochemical environment. In order to examine this concept we return to the dissociation of $\text{H}_2\text{S}(\text{aq})$ represented by

equations 9.30 and 9.31. However, here we rewrite the mass-action equations (9.32 and 9.33) as follows:

$$\frac{[\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{10^{-7.0}}{[\text{H}^+]} \quad (9.75)$$

and:

$$\frac{[\text{S}^{2-}]}{[\text{HS}^-]} = \frac{10^{-12.9}}{[\text{H}^+]} \quad (9.76)$$

We see that the activity ratios of $[\text{HS}^-]/[\text{H}_2\text{S}]$ and $[\text{S}^{2-}]/[\text{HS}^-]$ depend on the activity of the hydrogen ion. According to equation 9.75, $[\text{HS}^-]/[\text{H}_2\text{S}] = 1.0$ when $[\text{H}^+] = 10^{-7.0}$ mol/L. If $[\text{H}^+] > 10^{-7.0}$, say $10^{-6.0}$, then $[\text{HS}^-]/[\text{H}_2\text{S}] = 0.1$, which means that the activity of H_2S is 10 times greater than the activity of $[\text{HS}^-]$. Similarly, if $[\text{H}^+] < 10^{-7.0}$, say $10^{-8.0}$, then $[\text{HS}^-]/[\text{H}_2\text{S}] = 10$ and $[\text{HS}^-]$ is 10 times greater than that of H_2S . Evidently, $[\text{H}^+] = 10^{-7.0}$ (pH = 7.0) is an important boundary at which the abundances of H_2S and HS^- are equal. H_2S dominates at pH < 7.0, whereas HS^- dominates at pH > 7.0.

Similar arguments, applied to equation 9.76, indicate that pH = 12.9 is another boundary in the system. At pH < 12.9 we find that HS^- is more abundant than S^{2-} , whereas at pH > 12.9 the sulfide ion (S^{2-}) dominates. Such relationships occur in all weak acids and bases because their dissociation into ions is controlled by the pH of the environment.

The control of dissociation equilibria by the pH has an important consequence because it means that we can identify the dominant ions at different values of the pH. In order to demonstrate how this works we fix the total amount of sulfur-bearing species in the solution at 10^{-2} mol/L and calculate the activities of H_2S , HS^- , and S^{2-} as a function of pH. At pH = 6.0 we obtain from equation 9.75:

$$[\text{H}_2\text{S}] = \frac{10^{-6.0} [\text{HS}^-]}{10^{-7.0}} = 10 [\text{HS}^-] \quad (9.77)$$

and from equation 9.76:

$$[\text{S}^{2-}] = \frac{10^{-12.9} [\text{HS}^-]}{10^{-6.0}} = 10^{-6.9} [\text{HS}^-] \quad (9.78)$$

From the mass balance:

$$(\text{H}_2\text{S}) + (\text{HS}^-) + (\text{S}^{2-}) = 1 \times 10^{-2} \text{ mol/L} \quad (9.79)$$

If all activity coefficients are equal to one, we can substitute equations 9.77 and 9.78 into 9.79, obtaining:

$$10[\text{HS}^-] + [\text{HS}^-] + 10^{-6.9}[\text{HS}^-] = 1 \times 10^{-2} \text{ mol/L} \quad (9.80)$$

which reduces to:

$$11[\text{HS}^-] = 1 \times 10^{-2} \text{ mol/L} \quad (9.81)$$

and hence $[\text{HS}^-] = 9.09 \times 10^{-4}$ mol/L. From equation 9.77 we determine that $[\text{H}_2\text{S}] = 9.09 \times 10^{-3}$ mol/L and from 9.78 we have $[\text{S}^{2-}] = 1.14 \times 10^{-10}$ mol/L. Therefore, H_2S is the most abundant species at pH = 6.0 and constitutes 90.9% of all S-bearing ions or molecules in the solution. The bisulfide ion (HS^-) is next in abundance with 9.09%, which leaves only 0.01% for S^{2-} . When we repeat this calculation for different values of the pH, we generate three curves that represent the changing abundances of H_2S , HS^- , and S^{2-} in the solution. As expected, we see from Figure 9.3 that H_2S dominates at pH < 7.0, that HS^- is the dominant ion for pH values from 7.0 to 12.9, and that S^{2-} is dominant at pH > 12.9. Although all of the ions or molecules are present throughout the range of pH values, most of the S in the solution is associated with a particular species except at the boundaries at which the abundances of two species are equal.

9.6 Solubility of Amorphous Silica

The oxides of many metals react with water to form bases and the oxides of nonmetals react with water to form acids. For example, CO_2 reacts with water to form carbonic acid:



and SO_2 forms hydrosulfurous acid:



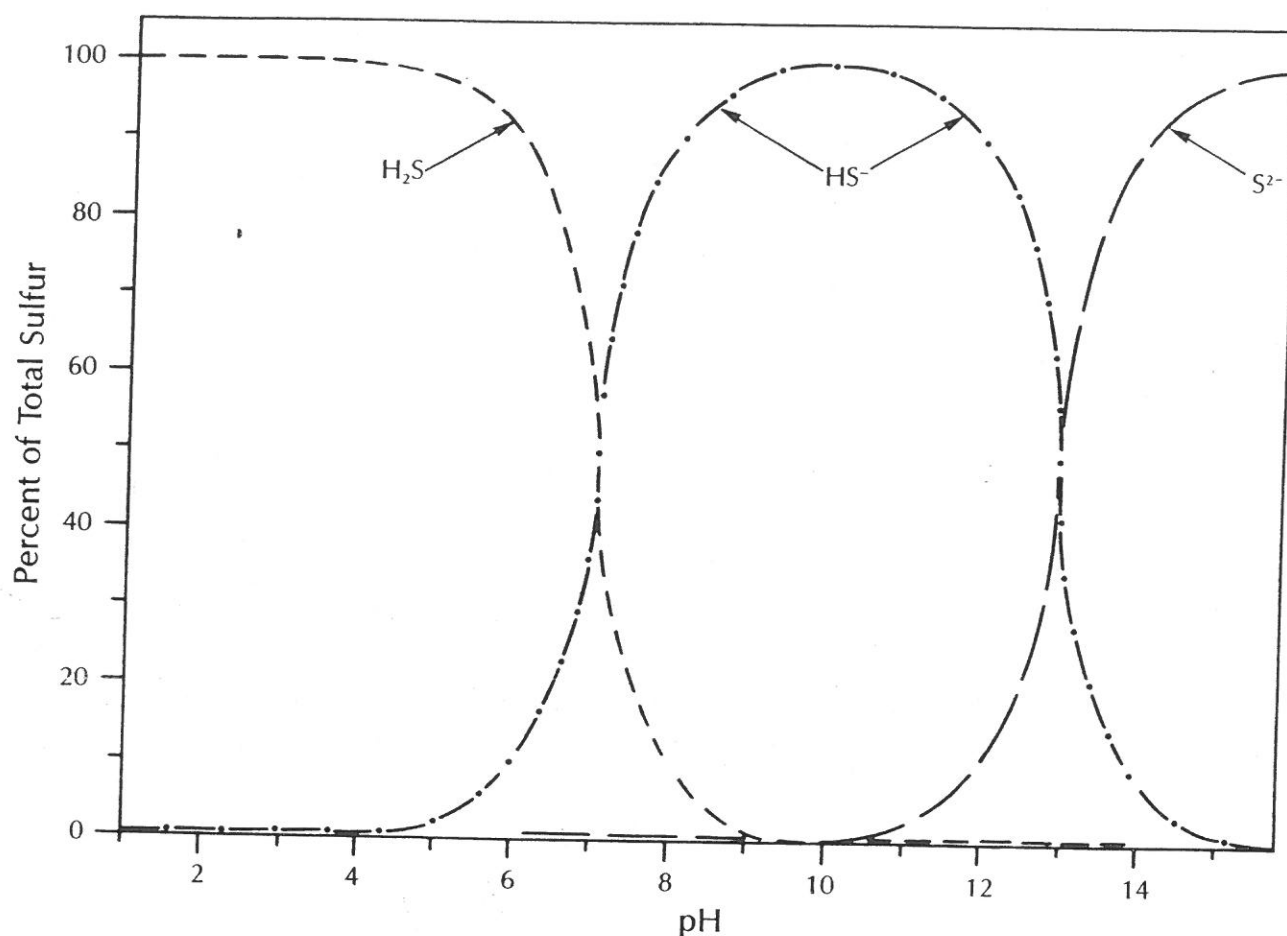
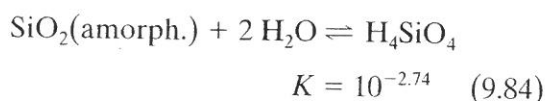


Figure 9.3 The pH dependence of the abundances of S-bearing ions and molecules in a solution of $\text{H}_2\text{S}(\text{aq})$ containing a fixed amount of S in solution (equation 9.79). Note that H_2S is dominant at $\text{pH} < 7.0$, HS^- dominates between $\text{pH} = 7.0$ and 12.9 , and that S^{2-} is dominant only at $\text{pH} > 12.9$. However, all of the ions are present at all pH values even though their abundances may be small compared to that of the dominant ion.

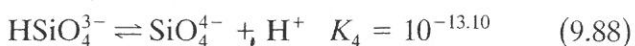
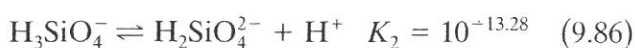
In a very similar manner, silicon dioxide reacts with water to form silicic acid, such that at equilibrium:



SiO_2 is a solid compound that can either be amorphous or assume several different polymorphic crystalline forms, including quartz, cristobalite, and tridymite. Silicic acid actually forms as a result of chemical weathering of the common rock-forming aluminosilicate minerals such as the feldspars and micas rather than by solution of crystalline or amorphous SiO_2 . However, when its solubility is exceeded, it forms amorphous silica, which

settles out slowly as a gelatinous precipitate (Iler, 1979). Given sufficient time, the precipitate expels water and begins to crystallize, forming *opal A* and *opal CT* as intermediate phases (Kastner et al., 1977). The process ends with the crystallization of a cryptocrystalline variety of quartz called *chalcedony*, which forms *chert* or *flint* and occurs in *geodes* as *agate*. Quartz is highly insoluble, and dissolves in water only sparingly, even during long periods of geologic time. Amorphous silica, however, is much more reactive and generally maintains equilibrium with silicic acid.

We are now in a position to discuss the solubility of amorphous silica based on equation 9.84 and on the dissociation of the silicic acid:



When amorphous silica and pure water have reached equilibrium at 25°C (equation 9.84), the activity of silicic acid is given by the Law of Mass Action:

$$[\text{H}_4\text{SiO}_4] = 10^{-2.74} \text{ mol/L} \quad (9.89)$$

The equilibrium (equation 9.84) is *independent* of the pH; therefore, the activity of $[\text{H}_4\text{SiO}_4]$ in a saturated solution of silicic acid in contact with solid amorphous SiO_2 is *constant* and varies only with temperature. The dissociation constants of silicic acid are all very small, making this a very weak acid. We can calculate the degree of dissociation of silicic acid at pH = 7.0 by proceeding stepwise from equation 9.85:

$$\frac{[\text{H}^+][\text{H}_3\text{SiO}_4^-]}{[\text{H}_4\text{SiO}_4]} = 10^{-9.71} \quad (9.90)$$

$$\begin{aligned} [\text{H}_3\text{SiO}_4^-] &= \frac{10^{-9.71} \times 10^{-2.74}}{10^{-7.0}} \\ &= 10^{-5.45} \text{ mol/L} \end{aligned} \quad (9.91)$$

$$\begin{aligned} D_1 &= \frac{10^{-5.45} \times 10^2}{10^{-2.74}} \\ &= 0.19\% \end{aligned} \quad (9.92)$$

Therefore, the activity of H_3SiO_4^- at pH = 7.0 is about 500 times less than that of H_4SiO_4 and does not contribute appreciably to the solubility of amorphous SiO_2 .

At pH = 8.0 the activity of H_3SiO_4^- increases to $10^{-4.45}$ mol/L (equation 9.91) and D_1 rises to 1.95%. At pH = 9.0 $[\text{H}_3\text{SiO}_4^-]$ increases to $10^{-3.45}$ mol/L and D_1 reaches 19.5%. We see that the degree of dissociation of silicic acid is very low at pH < 8.0 and rises rapidly as the pH increases above that value. As a result, the solubility of amorphous silica also rises because it is based on the *sum*

of the concentrations of the Si-bearing ions in solution. The first dissociation step (equation 9.85) makes the largest contribution to the increase in the solubility of SiO_2 (amorphous) with increasing pH. The other ions come into play only in extremely basic solution.

The solubility of amorphous silica as a function of pH is shown graphically in Figure 9.4. Note that the concentration is expressed in milligrams per liter (mg/L) of SiO_2 because it is commonly stated this way in chemical analyses of water. The SiO_2 is not actually present in molecular form but represents H_4SiO_4 to which it can be related by equation 9.84. Therefore, the concentration of SiO_2 stated in milligrams per liter can be recalculated as H_4SiO_4 in moles per liter by the following consideration. If $\text{SiO}_2 = 25.0$ mg/L, its molar concentration is $25.0/60.08$ mmol/L or 0.416×10^{-3} mol/L, where 60.08 is the molecular weight of SiO_2 . Equation 9.84 indicates that for every mole of amorphous SiO_2 that dissolves 1 mol of H_4SiO_4 is produced. Therefore, since 0.416×10^{-3} mol of SiO_2 dissolved to give a concentration of 25.0 mg/L, the concentration of H_4SiO_4 in that solution is also 0.416×10^{-3} or 4.16×10^{-4} mol/L.

The concentration of SiO_2 in Figure 9.4 is plotted on a linear rather than a logarithmic scale in order to emphasize that the solubility of amorphous SiO_2 at 25°C increases steeply at pH > 8 because of the dissociation of H_4SiO_4 to H_3SiO_4^- , which introduces additional Si-bearing ions into the water. Therefore, even a small *decrease* in the pH of *basic* solutions containing H_4SiO_4 may *reduce* the solubility of SiO_2 enough to saturate the solution and to cause amorphous SiO_2 to be deposited. For example, a decrease of 0.1 pH units from 8.5 to 8.4 of a *saturated* solution can result in the deposition of 1.37 mg of amorphous SiO_2 per liter of solution. Such seemingly small amounts quickly increase when we apply them to the large volume of groundwater that may flow through an aquifer in the course of geologic time. Subtle changes in the geochemical environment can be magnified by time into large-scale transformations.

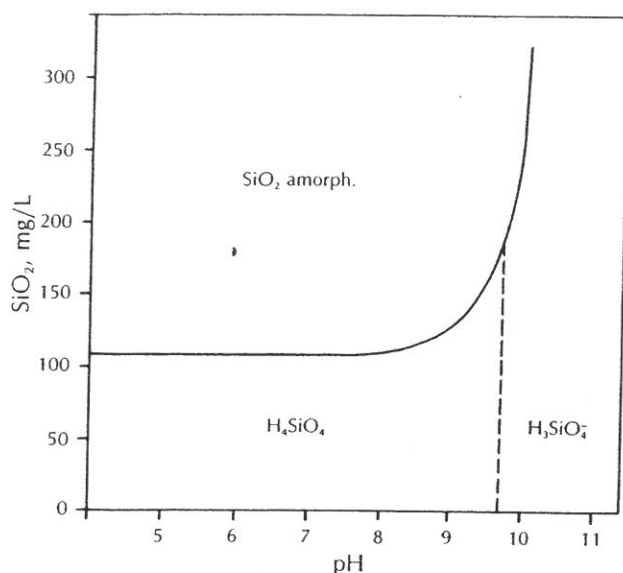
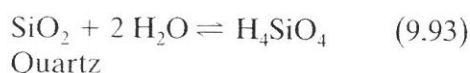


Figure 9.4 Solubility of amorphous SiO_2 expressed in units of mg of SiO_2 per liter of pure water at 25°C based on equations 9.84 and 9.85. Note that H_4SiO_4 begins to dissociate appreciably at about $\text{pH} = 8.0$ and that H_3SiO_4^- becomes dominant at $\text{pH} = 9.71$. The second dissociation (equation 9.85) is negligible in the pH range shown here and, at $\text{pH} = 10.0$, it increases the solubility of amorphous SiO_2 by only 0.03%. Silicic acid is derived primarily by chemical weathering of the common rock-forming Al-silicate and silicate minerals, but may be precipitated from saturated solutions as gelatinous amorphous silica when the pH decreases. As amorphous silica ages, it recrystallizes to form opal A and opal CT until it ultimately forms chalcedony, which is a variety of quartz.

Surprisingly, quartz is not an important source of silicic acid in natural solution because it is quite insoluble. The equilibrium constant of the reaction:



is $K = 10^{-4.01}$. As a result, the activity of H_4SiO_4 in a saturated solution in contact with quartz at 25°C is $9.76 \times 10^{-5} \text{ mol/L}$, which is equivalent to 5.9 mg/L of SiO_2 in solution. The concentrations of Si in average river water and seawater (Table 4.7) are 6.5 and 2.8 $\mu\text{g/g}$, respectively. These concentrations can be transformed into SiO_2 in milligrams

per liter by converting first to micromoles of Si and then to micrograms of SiO_2 . For average river water:

$$\text{SiO}_2 = \frac{6.5 \times 60.08 \times 10^3}{28.086 \times 10^3} = 13.9 \text{ mg/L} \quad (9.94)$$

Therefore, average river water is *supersaturated* with respect to quartz but is undersaturated with respect to amorphous silica. However, quartz does not precipitate from aqueous solutions directly but forms only by recrystallization of amorphous SiO_2 as discussed previously. The concentration of SiO_2 in seawater is 5.8 mg/L (assuming a density of 1.025 g/cm^3), which is close to the solubility of quartz at 25°C . Seawater has a lower concentration of SiO_2 than river water because certain organisms (sponges, diatoms, and radiolarians) form skeletons composed of opal A. When these organisms die, their siliceous skeletons accumulate on the bottom of the ocean and may ultimately form either chert, composed of cryptocrystalline quartz, or deposits of diatomite (Cressman, 1962; Wedepohl, 1972).

The geochemistry of silica illustrates the point that some reactions in nature are essentially *irreversible*. When NaCl dissolves in water the reaction is *reversible* because the compound does precipitate from supersaturated solutions. When amorphous silica dissolves in water, it can be made to precipitate again, although with some difficulty. However, when quartz dissolves in water at 25°C to form silicic acid, the reaction cannot be reversed at the same temperature. We will encounter this phenomenon again in Chapter 10 when we discuss the solubility of minerals, some of which form only by crystallization of magma at elevated temperatures.

9.7 Summary

Chemical reactions have a natural tendency to achieve a state of equilibrium in which the rates of the forward and backward reactions are equal. As a result, the amounts of reactants and products that coexist at equilibrium are invariant with time. This observational evidence was originally used to

formulate the Law of Mass Action, which was later derived from the principles of thermodynamics.

Chemical reactions in the natural environment may fail to reach equilibrium because the products escape from the site of the reaction or because reactions involving the transformation of one solid into another are very slow. In addition, some natural reactions are irreversible.

Acids and bases are defined as compounds that release H^+ or OH^- ions in aqueous solutions, respectively. The bases of some elements are amphoteric and act like bases in acidic environments and like acids in basic environments. Weak acids and bases dissociate only partially depending on the pH of the environment. In general, the pH of natural environments results from the com-

bined effect of all chemical reactions that are taking place simultaneously.

Some bases are insoluble and actually occur as minerals in nature. For example, $Mg(OH)_2$ forms the mineral brucite. The solubility of such insoluble bases can be calculated by solving a set of simultaneous equations derived from the Law of Mass Action and from the requirement of conservation of mass and electrical charge.

Weak acids play an important role in geochemistry because the abundances of the ions they form by dissociation are controlled by the pH of the environment. This phenomenon affects the solubility of amorphous silica, which increases rapidly at $pH > 8$ because of the dissociation of silicic acid.

Problems

1. If the concentration of an ion in a solution is 5.0×10^{-2} mol/L at $25^\circ C$, what is its concentration in the same solution at $45^\circ C$? Use the data in Table 9.1.
(Answer: 4.96×10^{-2} mol/L)

2. Derive a relationship between the molarity (M), the formality (F), and the density (d) of a solution.

3. Calculate the normality of hydrochloric acid (HCl) from the following information provided by the label on the bottle. Assay: 37%; net weight: 2.72 kg; molecular weight: 36.46; specific gravity: 1.18.
(Answer: 12.0)

4. Calculate the normality of sulfuric acid (H_2SO_4) based on the information provided by the label on the

bottle. Assay: 98.0%; net weight: 4.08 kg; molecular weight: 98.08; specific gravity: 1.84. (Answer 36.8)

5. What volume of 35 N (normal) H_2SO_4 is required to make 250 mL of 1.5 N H_2SO_4 ?

6. Calculate the pH of hydrofluoric acid containing 0.1 mol of HF per liter of solution. Find the dissociation constant in Table 9.3.

7. Calculate the activities of all ions and the pH of a solution containing 0.1 mol of phosphoric acid per liter of solution. Find the equilibrium constants in Table 9.3.

8. Calculate the solubility of gibbsite ($Al(OH)_3$) at $pH = 5.0$. Find the dissociation constants in Table 9.3.

References

- CRESSMAN, E. R., 1962. Nondetrital siliceous sediments. Chapter T. 1-23. In M. Fleischer (Ed.), *Data of Geochemistry*, U.S. Geol. Surv. Paper 440-T.
- DREVER, J. I., 1988. *The Geochemistry of Natural Waters*, 2nd ed. Prentice-Hall, Upper Saddle River, NJ, 435 pp.
- GARRELS, R. M., and C. L. CHRIST, 1965. *Minerals, Solutions and Equilibria*. Harper & Row, New York, 450 pp.
- ILER, R. K., 1979. *The Chemistry of Silica*. Wiley, New York, 866 pp.
- KASTNER, M., J. B. KEENE, and J. M. GIESKES, 1977. Diagenesis of siliceous oozes—I. Chemical controls on the rate of opal A and opal CT transformation: an experimental study. *Geochim. Cosmochim. Acta*, **41**:1041-1060.

- KRAUSKOPF, K. B., 1979. *Introduction to Geochemistry*, 2nd ed. McGraw-Hill, New York, 617 pp.
- LINDSAY, W. L., 1979. *Chemical Equilibria in Soils*. Wiley, New York, 449 pp.
- MOORE, W. J., 1955. *Physical Chemistry*, 2nd ed. Prentice-Hall, Upper Saddle River, NJ, 633 pp.
- STUMM, W., and J. J. MORGAN, 1970. *Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters*. Wiley, New York, 583 pp.
- WEAST, R. C., M. J. ASTLE, and W. H. BEYER (Eds.), 1986. *CRC Handbook of Chemistry and Physics*, 66th ed. CRC Press, Boca Raton, FL.
- WEDEPOHL, K. H. (Ed.), 1972. *Silicon. Handbook of Geochemistry*, vol. II-2. Springer-Verlag, Berlin.

Salts and Their Ions

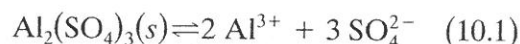
When an acid and a base are mixed, the hydrogen ion of the acid combines with the hydroxyl ion of the base to form water. The remaining anion of the acid and the cation of the base form a salt, which may precipitate or remain in solution depending on its solubility. Salts are named after the acids that provided the anions. For example, hydrochloric acid forms *chlorides*, sulfuric acid forms *sulfates*, carbonic acid forms *carbonates*, and silicic acid forms *silicates*. The naturally occurring salts of these and other acids are *minerals* that form the rocks of the crust of the Earth. The only minerals that are not salts are the *oxides*, *hydroxides*, and *native elements*. Evidently, the study of salts and their properties is an important subject in geochemistry. In this chapter we will study the solubility of salts in water and the interactions of the resulting ions with molecules of water.

10.1 Solubility of Salts

When salts dissolve in water, they dissociate into the anions and cations of the acid and the base from which they were derived. Neutral molecules of salts may also form, but their abundance is low in most cases. When a salt has formed a *saturated* solution, a state of equilibrium exists between the ions in the solution and any excess salt remaining in the solid state. Therefore, the Law of Mass Action applies and can be used to calculate the activities of the ions in a saturated solution and hence the solubility of the salt.

We choose aluminum sulfate $[\text{Al}_2(\text{SO}_4)_3]$ to illustrate how the Law of Mass Action can be used for this purpose. Aluminum sulfate, a salt of

sulfuric acid and aluminum hydroxide, is quite soluble in water and dissociates readily into ions:



We assume for the time being that these ions do not interact with water, that this reaction is the only source of Al^{3+} and SO_4^{2-} ions, that no other ions are present, and that the water temperature is 25°C . We see from equation 10.1 that each mole of aluminum sulfate that dissolves produces two moles of Al^{3+} and three moles of SO_4^{2-} in the solution. Therefore, if x is the number of moles of salt that dissolve in a saturated solution, the concentrations of the resulting ions will be $(\text{Al}^{3+}) = 2x$ and $(\text{SO}_4^{2-}) = 3x$. According to the Law of Mass Action (equation 9.13):

$$[\text{Al}^{3+}]^2[\text{SO}_4^{2-}]^3 = K_{\text{sp}} \quad (10.2)$$

where K_{sp} is the *solubility product constant*, and the activity of excess solid aluminum sulfate is equal to one. If the concentrations of the ions are equal to the activities in the solution, $[\text{Al}^{3+}] = 2x$ and $[\text{SO}_4^{2-}] = 3x$. Substituting into the equation 10.2 we obtain:

$$(2x)^2(3x)^3 = K_{\text{sp}} \quad (10.3)$$

where $K_{\text{sp}} = 69.19$ (calculated from its solubility given by Weast et al., 1986). The solubility product constant is a large number, indicating that aluminum sulfate is, in fact, a very soluble salt. For this reason, it does not occur naturally as a mineral. Equation 10.3 reduces to $108x^5 = 69.19$, which yields $x = 0.9147$. Therefore, a saturated solution of aluminum sulfate contains $2x = 1.829$ mol/L of Al^{3+} and $3x = 2.744$ mol/L of SO_4^{2-} . The Al^{3+} reacts with water to form insoluble Al hydroxide.

The amount of aluminum sulfate that dissolves in a saturated solution is equal to $x = 0.9147 \text{ mol/L}$. Since the molecular weight of aluminum sulfate is 342.1478, its solubility is $0.9147 \times 342.1478 = 3.13 \times 10^2 \text{ g/L}$ of water.

Most minerals are much less soluble in water than aluminum sulfate, and their solubility product constants have correspondingly smaller values. Table 10.1 contains the solubility product constants of some common minerals taken primarily from a compilation by Krauskopf (1979) but augmented with data from Lindsay (1979). These constants can be used to calculate the activities of the ions in saturated solutions of minerals by means of the Law of Mass Action.

We are also interested in finding out whether a solution is actually saturated with respect to a specific mineral. For example, if a sample of water contains $5.00 \times 10^{-2} \text{ mol/L}$ of Ca^{2+} and $7.00 \times 10^{-3} \text{ mol/L}$ of SO_4^{2-} , we may want to know whether this solution is saturated with respect to calcium sulfate (anhydrite). In order to find out, we first write the equation to represent the dissociation of CaSO_4 into its ions:



At equilibrium the Law of Mass Action applies; thus:

$$[\text{Ca}^{2+}][\text{SO}_4^{2-}] = 10^{-4.5} \quad (10.5)$$

If the solution is saturated with respect to anhydrite, the product of activities of the ions in the solution must equal $10^{-4.5}$. We assume for the sake of argument that the measured concentrations are equal to the activities of the ions and therefore calculate the *ion activity product* (IAP):

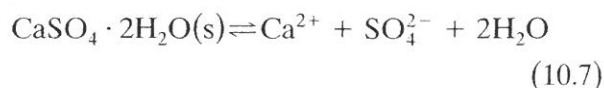
$$\begin{aligned} (5.00 \times 10^{-2})(7.00 \times 10^{-3}) &= 35.00 \times 10^{-5} \\ &= 10^{-3.45} \end{aligned} \quad (10.6)$$

Since the IAP ($10^{-3.45}$) in this case is *larger* than the solubility product constant, the solution is *supersaturated* with respect to calcium sulfate. Therefore, anhydrite should *precipitate*. If the IAP is found to be *less* than the solubility product

constant, the solution is *undersaturated* and therefore can *dissolve* the mineral. If $\text{IAP} = K_{\text{sp}}$, the solution is *saturated* and a state of equilibrium exists between the solid and its ions.

In the case we are considering, it turns out that CaSO_4 does *not* actually precipitate from a supersaturated solution of its ions. Instead, *gypsum* ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) forms and subsequently crystallizes to anhydrite. This is another example of the *irreversibility* of some geochemical reactions we first mentioned in Section 9.6. In this case, CaSO_4 dissolves in water but does *not* precipitate at 25°C . Similarly, most silicate minerals dissolve in water but do not precipitate from aqueous solutions of their ions at low temperature. Some silicate minerals precipitate from aqueous solutions only at elevated temperatures or require a specific starting material like volcanic glass, and the silicate minerals of igneous rocks crystallize only from silicate melts at temperatures close to 1000°C .

In the case of the calcium sulfate solution we are considering, *gypsum* precipitates until the activities of the ions are reduced sufficiently so that the IAP is equal to K_{sp} and solid gypsum is in equilibrium with its ions:



Therefore, at equilibrium between gypsum and its ions:

$$[\text{Ca}^{2+}][\text{SO}_4^{2-}] = 10^{-4.6} \quad (10.8)$$

If x moles of gypsum precipitate, the activities of the ions at equilibrium will be:

$$[\text{Ca}^{2+}] = 5.00 \times 10^{-2} - x \quad (10.9)$$

$$[\text{SO}_4^{2-}] = 7.00 \times 10^{-3} - x \quad (10.10)$$

Substituting into equation 10.8 yields:

$$(5.00 \times 10^{-2} - x)(7.00 \times 10^{-3} - x) = 10^{-4.6} \quad (10.11)$$

which reduces to a quadratic equation:

$$x^2 - (5.7 \times 10^{-2})x + 3.25 \times 10^{-4} = 0 \quad (10.12)$$

Table 10.1 Solubility Product Constants for Different Salts at 25°C

$pK^{a,b}$		
Carbonates		
Ag_2CO_3		11.09 (L)
$BaCO_3$	witherite	8.3 (K) ^c
$CaCO_3$	calcite	8.35 (K)
$CaCO_3$	aragonite	8.22 (K)
$CaCO_3 \cdot 6H_2O$	ikaite	6.38 (L)
$CdCO_3$	otavite	13.7 (K), 12.0 (L)
$CoCO_3$	sphaerocobaltite	10.0 (K)
$CuCO_3$		9.63 (L)
$Cu_2(OH)_2CO_3$	malachite	33.8 (K), 33.2 (L)
$Cu_3(OH)_2(CO_3)_2$	azurite	66.5 (L)
$FeCO_3$	siderite	10.7 (K), 10.2 (L)
$HgCO_3$		22.6 (L)
Hg_2CO_3	$[Hg_2^{2+}][CO_3^{2-}]$	14.0 (L)
$MgCO_3$	magnesite	7.5 (K), 7.46 (L)
$MgCO_3 \cdot 3H_2O$	nesquehonite	5.6 (K), 4.67 (L)
$MgCO_3 \cdot 5H_2O$	lansfordite	4.54 (L)
$MgCa(CO_3)_2$	dolomite	17.9 (L)
$MnCO_3$	rhodochrosite	9.3 (K), 10.1 (L)
$NiCO_3$		6.9 (K)
$PbCO_3$	cerussite	13.1 (K), 13.5 (L)
$Pb_2CO_3Cl_2$	phosgenite	20.0 (L)
$Pb_3(CO_3)_2(OH)_2$		46.8 (L)
$SrCO_3$	strontianite	9.0 (K) ^c
UO_2CO_3	$[UO_2^{2+}][CO_3^{2-}]$	10.6 (K)
$ZnCO_3$	smithsonite	10.0 (20°C, K), 10.2 (L)
Sulfates		
Ag_2SO_4		4.81 (K, L)
$KAl_3(SO_4)_2(OH)_6$	alunite	80.95 (L)
$BaSO_4$	barite	10.0 (K)
$CaSO_4$	anhydrite	4.5 (K), 4.41 (L)
$CaSO_4 \cdot 2H_2O$	gypsum	4.6 (K), 4.63 (L)
$CdSO_4$		0.044 (L)
$CdSO_4 \cdot 2H_2O$		1.59 (L)
$CuSO_4$		-3.72 (L)
$CuSO_4 \cdot 5H_2O$		2.61 (L)
$Cu_4(OH)_6SO_4$	brochantite	68.6 (L)
$FeSO_4$		-2.65 (L)
$FeSO_4 \cdot 7H_2O$		2.46 (L)
$Fe_2(SO_4)_3$		-2.89 (L)
$KFe_3(SO_4)_2(OH)_6$	jarosite	96.5 (L)
$HgSO_4$		3.34 (L)
Hg_2SO_4		6.20 (L)
$MgSO_4$		-8.18 (L)
$MnSO_4$		-3.43 (L)
$MnSO_4 \cdot H_2O$		-0.47 (L)

Table 10.1 (continued)

		$pK^{a,b}$
$Mn_2(SO_4)_3$		11.6 (L)
$PbSO_4$	anglesite	7.8 (K), 7.79 (L)
$SrSO_4$	celestite	6.5 (K)
$ZnSO_4$	zinkosite	-3.41 (L)
Sulfides		
$\alpha\text{-Ag}_2\text{S}$		49.01 (L)
$\beta\text{-Ag}_2\text{S}$		48.97 (L)
Ag_2S		50.1 (K)
Bi_2S_3	bismuthinite	100.0 (K)
CaS	oldhamite	0.78 (L)
CdS	greenockite	27.0 (K, L)
$CoS(\alpha)$		21.3 (K)
$CoS(\beta)$		25.6 (K)
Cu_2S	chalcocite	48.5 (K, L)
CuS	covellite	36.1 (K)
$\alpha\text{-Fe}_{0.95}\text{S}$	pyrrhotite	17.4 (L)
$\alpha\text{-FeS}$	troilite	16.2 (L)
FeS	troilite	18.1 (K)
FeS_2	pyrite	42.5 (L)
FeS_2	marcasite	41.8 (L)
Fe_2S_3		88.0 (L)
$\alpha\text{-HgS}$	cinnabar (red)	53.0 (K), 52.0 (L)
$\beta\text{-HgS}$	metacinnabar (black)	52.7 (K), 51.7 (L)
Hg_2S	$[Hg_2^{2+}][S^{2-}]$	54.8 (L)
MgS		-5.59 (L)
MnS	(green)	13.5 (K), 11.7 (L)
MnS	(pink) alabandite	10.5 (K), 12.8 (L)
MnS_2	haurite	81.4 (L)
MoS_2	molybdenite	?
$\alpha\text{-NiS}$		19.4 (K)
$\gamma\text{-NiS}$		26.6 (K)
PbS	galena	17.5 (K, L)
Sb_2S_3	stibnite	90.8 (K)
SnS		25.9 (K) ^c
$\alpha\text{-ZnS}$	sphalerite	24.7 (K, L)
$\beta\text{-ZnS}$	wurtzite	22.5 (K, L)
Phosphates		
Ag_3PO_4		16.0 (L)
$AlPO_4$	berlinite	19.0 (L)
$AlPO_4 \cdot 2H_2O$	variscite	22.1 (K, L)
$H_6K_3Al_3(PO_4)_8 \cdot 18H_2O$	K-taranakite	178.7 (L)
$CaHPO_4 \cdot 2H_2O$	brushite	6.57 (K, L)
$CaHPO_4$	monetite	6.89 (L)
$\alpha\text{-Ca}_3(PO_4)_2$		25.5 (L)
$\beta\text{-Ca}_3(PO_4)_2$	whitlockite	28.7 (K), 28.9 (L)

Table 10.1 (continued)

		pK ^{a,b}
$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$	octacalcium phosphate	80.6 (L)
$\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$	fluorapatite	119.2 (L)
$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$	hydroxyapatite	116.4 (L)
$\text{Cd}_3(\text{PO}_4)_2$		38.1 (L)
$\text{Cu}_3(\text{PO}_4)_2$		36.9 (K, L)
$\text{Cu}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$		38.8 (L)
FePO_4 (amorph.)		21.6 (K)
$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	strengite	26.4 (K, L)
$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	vivianite	36.0 (L)
Hg_2HPO_4		12.4 (L)
KH_2PO_4		0.21 (L)
K_2HPO_4		-3.60 (L)
$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	newberyite	5.82 (L)
$\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$		10.6 (L)
$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$	struvite	13.2 (L)
$\text{Mg}_3(\text{PO}_4)_2$		25.2 (K), 14.6 (L)
$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	bobierite	25.0 (L)
$\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$		23.1 (L)
MnHPO_4		12.9 (L)
$\text{Mn}_3(\text{PO}_4)_2$		27.4 (L)
PbHPO_4		11.4 (K), 11.5 (L)
$\text{Pb}(\text{H}_2\text{PO}_4)_2$		114.7 (L)
$\text{Pb}_3(\text{PO}_4)_2$		43.5 at 38°C (K), 44.4 (L)
$\text{Pb}_3(\text{PO}_4)_3\text{Br}$	bromopyromorphite	78.2 (L)
$\text{Pb}_3(\text{PO}_4)_3\text{Cl}$	chloropyromorphite	83.7 (L)
$\text{Pb}_3(\text{PO}_4)_3\text{F}$	fluoropyromorphite	71.6 (L)
$\text{Pb}_3(\text{PO}_4)_3\text{OH}$	hydroxypyromorphite	76.8 (L)
$(\text{UO}_2)_3(\text{PO}_4)_2$	$[\text{UO}_2^{2+}]^3[\text{PO}_4^{3-}]^2$	49.7 (K)
UO_2HPO_4	$[\text{UO}_2^{2+}][\text{HPO}_4^{2-}]$	12.2 (K)
$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	hopeite	35.3 (L)
$\text{Zn}_3(\text{PO}_4)_2$		35.3 (K)
Molybdates		
Ag_2MoO_4		11.55 (L)
CaMoO_4	powellite	7.94 (L)
CuMoO_4		6.48 (L)
FeMoO_4		7.70 (L)
MgMoO_4		0.62 (L)
MnMoO_4		4.13 (L)
PbMoO_4	wulfenite	16.0 (L)
ZnMoO_4		4.49 (L)
Chlorides		
AgCl	cerargyrite	9.75 (K, L)
CuCl		6.7 (K)
PbCl_2	cotunnite	4.8 (K)
Hg_2Cl_2	$[\text{Hg}_2^{2+}][\text{Cl}^-]^2$	17.9 (K)

Table 10.1 (continued)

		$pK^{a,b}$
Fluorides		
AgF		100.0 (L)
BaF ₂		5.8 (K)
CaF ₂	fluorite	10.4 (K)
MgF ₂	sellaite	8.2 (K) ^c
PbF ₂		7.5 (K)
SrF ₂		8.5 (K)

^aExpressed as $-\log K_{sp}$.^bK = Krauskopf (1979), pp. 552–553; L = Lindsay (1979), calculated from standard free energies.^cUncertain by more than 0.8 (Krauskopf, 1979).

We solve this equation by means of the quadratic formula (equation 9.18) and obtain two roots: $x_1 = 5.05 \times 10^{-2}$ and $x_2 = 6.45 \times 10^{-3}$. We choose x_2 because x_1 reduces $[\text{SO}_4^{2-}]$ in equation 10.10 to a negative value. Therefore, the amount of gypsum that will precipitate *per liter* of solution is $6.45 \times 10^{-3} \times 172.17 = 1.11$ g. When equilibrium has been established after gypsum has precipitated, the IAP $(5.00 - 0.645) \times 10^{-2} \times (7.00 - 6.45) \times 10^{-3} = 10^{-4.6}$, as required for equilibrium. Note that the $[\text{Ca}^{2+}]/[\text{SO}_4^{2-}]$ ratio has increased by more than a factor of 10 from its initial value of $(5.00 \times 10^{-2})/(7.00 \times 10^{-3}) = 7.1$ to $(4.35 \times 10^{-2})/(0.055 \times 10^{-2}) = 79.2$. Evidently, the precipitation of a salt from a supersaturated solution not only reduces the concentrations of the ions but actually *changes the chemical composition* of the remaining solution.

If gypsum continues to precipitate from this solution, the activity of SO_4^{2-} approaches zero and the $[\text{Ca}^{2+}]/[\text{SO}_4^{2-}]$ ratio rises toward infinity. This phenomenon, which is illustrated in Figure 10.1, occurs during the evolution of brines by evaporative concentration and constitutes a *geochemical divide*. The solution we have been discussing is depleted in sulfate and is enriched in Ca^{2+} by the progressive precipitation of gypsum because its initial molar $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio was greater than one. If $\text{Ca}^{2+}/\text{SO}_4^{2-} < 1.0$, precipitation of gypsum causes depletion in Ca^{2+} and enrichment in sulfate. Therefore, the value of the molar $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio of a solution from which gypsum precipitates deter-

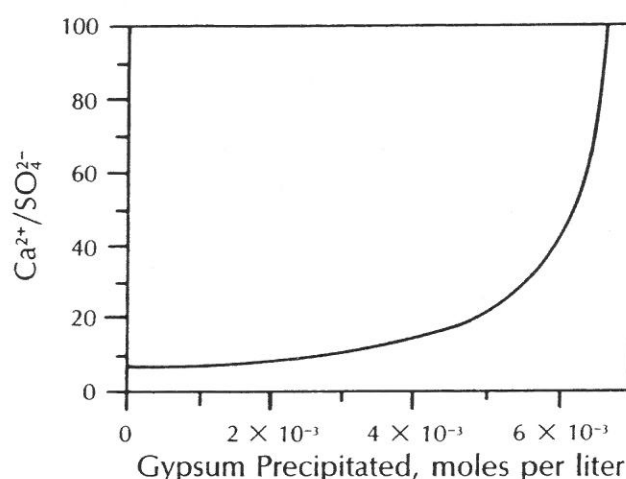
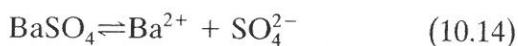
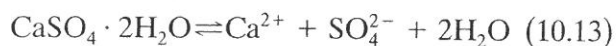


Figure 10.1 Changes in the molar $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio of a solution from which gypsum is precipitating based on equations 10.9 and 10.10. In this example, the solution contains more Ca^{2+} than SO_4^{2-} , and its $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio therefore *increases* as equal amounts of Ca^{2+} and SO_4^{2-} are removed from it. As a result, the solution becomes enriched in Ca^{2+} and depleted in SO_4^{2-} . If the solution initially contains more SO_4^{2-} than Ca^{2+} , it becomes enriched in SO_4^{2-} and depleted in Ca^{2+} as a result of progressive gypsum precipitation. This phenomenon constitutes a *geochemical divide* that affects the chemical evolution of brines by progressive evaporative concentration.

mines whether the solution becomes enriched in Ca^{2+} or SO_4^{2-} . Similar geochemical divides operate when other salts precipitate from isolated volumes of water undergoing evaporative concentration in a desert lake (Hardie and Eugster, 1970).

Natural water samples are much more complex than the solution we have been discussing because they contain a mixture of cations and anions and therefore may precipitate several different salts. For example, a solution may be saturated with respect to both gypsum and barium sulfate (barite). In this case we have two simultaneous equilibria with a common ion:



Both reactions contribute SO_4^{2-} ions to the solution, but the resulting activities must be the same for both equilibria. We can calculate the $[\text{Ca}^{2+}]/[\text{Ba}^{2+}]$ ratio of a solution that is saturated with respect to both gypsum and barite by applying the Law of Mass Action to equations 10.13 and 10.14:

$$[\text{Ca}^{2+}][\text{SO}_4^{2-}] = 10^{-4.6} \quad (10.15)$$

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = 10^{-10.0} \quad (10.16)$$

Since $[\text{SO}_4^{2-}]$ has the *same* value in both equilibria, we eliminate it by substituting $[\text{SO}_4^{2-}] = 10^{-4.6}/[\text{Ca}^{2+}]$ into equation 10.16:

$$\frac{[\text{Ba}^{2+}] \times 10^{-4.6}}{[\text{Ca}^{2+}]} = 10^{-10.0} \quad (10.17)$$

from which it follows that $[\text{Ba}^{2+}]/[\text{Ca}^{2+}] = 10^{-5.4}$ or $[\text{Ca}^{2+}]/[\text{Ba}^{2+}] = 2.5 \times 10^5$. Evidently, the activity of Ca^{2+} is 250,000 times that of Ba^{2+} when the solution is saturated with respect to both gypsum and barite.

We can determine the $[\text{SO}_4^{2-}]$ concentration of such a solution from the requirement for electrical neutrality:

$$2(\text{Ba}^{2+}) + 2(\text{Ca}^{2+}) + (\text{H}^+) = 2(\text{SO}_4^{2-}) + (\text{OH}^-) \quad (10.18)$$

From equations 10.15 and 10.16 we have, in terms of concentrations:

$$(\text{Ca}^{2+}) = \frac{10^{-4.6}}{\gamma_{\pm 2}[\text{SO}_4^{2-}]} \quad (10.19)$$

and:

$$(\text{Ba}^{2+}) = \frac{10^{-10.0}}{\gamma_{\pm 2}[\text{SO}_4^{2-}]} \quad (10.20)$$

where $\gamma_{\pm 2}$ is the activity coefficient of Ca^{2+} and Ba^{2+} defined by equation 9.12. By substituting into equation 10.18, setting $\gamma_{\pm 2} = 1.0$, and dropping (H^+) and (OH^-) , we obtain:

$$\frac{2 \times 10^{-4.6}}{[\text{SO}_4^{2-}]} + \frac{2 \times 10^{-10.0}}{[\text{SO}_4^{2-}]} = 2(\text{SO}_4^{2-}) \quad (10.21)$$

If we stipulate that $[\text{SO}_4^{2-}] = (\text{SO}_4^{2-})$, equation 10.21 reduces to:

$$10^{-4.6} + 10^{-10.0} = (\text{SO}_4^{2-})^2 \quad (10.22)$$

Evidently, the barite contributes a negligible amount of sulfate to the solution and $[\text{SO}_4^{2-}] = (\text{SO}_4^{2-}) = 10^{-2.3}$ mol/L.

The results of this calculation indicate that gypsum is able to force barite to precipitate when a saturated solution of barite comes in contact with gypsum. In other words, barite can replace gypsum or anhydrite because barite is less soluble than gypsum or anhydrite. The calcium sulfate can dissolve in a solution that is already saturated with respect to barite and thereby it can increase the sulfate concentration. As a result, the solution becomes *supersaturated* with respect to barite. Therefore, barite precipitates as gypsum or anhydrite dissolves until the $[\text{Ca}^{2+}]/[\text{Ba}^{2+}]$ ratio of the solution approaches 250,000 which is required for equilibrium. When that value is reached, the replacement of gypsum or anhydrite by barite stops.

Replacement of one mineral by another is a common phenomenon in geology and affects not only sulfates but also sulfide minerals, carbonates, and other types of compounds. In each case, the introduction of a common ion causes the solution to become supersaturated with respect to the *less soluble* compound. The effective ion may be the anion, as we have seen, or the cation itself. For example, if BaCl_2 , which is quite soluble, is added to a saturated solution of BaSO_4 , the sulfate precipitates until most of it is removed from the solution. In this case barite replaces BaCl_2 . The process always involves the replacement of the *more* soluble compound by the *less* soluble one.

Solutions in nature may become supersaturated with respect to a specific compound in several different ways, including (1) the introduction of a

common ion, as just described; (2) a change in the pH, exemplified in Chapter 9 by the precipitation of amorphous silica; (3) evaporative concentration of water in closed basins and in soil or sediment drying in the sun; and (4) temperature variations.

The solubility of compounds does depend on the temperature, but not always as we might expect. In general, solubilities *increase* with increasing temperature, but for some compounds the opposite is true. For example, the solubility of CaCO_3 and other carbonates *decreases* with increasing temperature because the solubility product constants of *calcite* and *aragonite* actually *decrease* with increasing temperature. We will take up the temperature dependence of the solubilities of minerals in Chapter 11 after we learn to calculate equilibrium constants from thermodynamic data.

10.2 Hydrolysis

Weak acids are only partly dissociated in water because the anion of the acid has a strong affinity for hydrogen ions. When a salt of a *weak acid* is dissolved in water, it releases anions into solution that have the same strong affinity for hydrogen ions. Therefore, these anions immediately bond to hydrogen ions and thereby form the parental acid. The hydrogen ions that bond with anions may already exist in the environment, or they may originate from the dissociation of water. In either case, when the salt of a weak acid is dissolved in water, the removal of H^+ causes the solution to become more basic.

The process we have just described is *hydrolysis*. It is defined as the interaction between water and one or both ions of a salt that results in the formation of the parental acid or base, or both. We can classify salts by the strength of the acid and base from which they form:

1. Strong acid + strong base.
2. Strong acid + weak base.
3. Weak acid + strong base.
4. Weak acid + weak base.

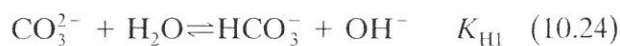
Salts derived from strong acids and strong bases (category 1), such as NaCl or CaSO_4 , do not hydrolyze because neither the anion nor the cation has a particular affinity for H^+ or for OH^- . Salts of strong acids and weak bases (category 2), such as FeCl_3 or CuSO_4 , release cations into solution that combine with OH^- to form the parental base. The removal of OH^- causes the solution to become more *acidic*. Salts of weak acids and strong bases (category 3) release anions that hydrolyze and make the solution more *basic*. Salts of weak acids and weak bases (category 4), like CuCO_3 or FeS_2 , release anions and cations both of which hydrolyze. In this case, the effect on the pH of a neutral solution must be determined by calculation because it depends on a comparison of the strengths of the parental acid and base.

Hydrolysis is a very important process because most of the common rock-forming minerals of the crust of the Earth are salts of *weak acids* and *strong bases*. For example, the carbonates and silicates of the alkali metals and alkaline earths are salts of this type. Therefore, the anions of these minerals split water molecules in order to form the weak parental acid and thereby cause the hydroxyl ion concentration of the solution to increase. This is why groundwater in carbonate aquifers is commonly basic. Even silicate minerals, such as the feldspars, hydrolyze when they interact with water by releasing Na^+ or K^+ from the surfaces of mineral grains and replacing it with H^+ .

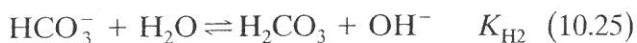
The dissociation of salts into ions and subsequent hydrolysis of the ions takes place very rapidly. As a result, these kinds of reactions are usually at equilibrium. Therefore, if we dissolve a small quantity of potassium carbonate in pure water at 25°C , it will dissolve completely and dissociate into ions:



The carbonate ions react with water to form bicarbonate:



The bicarbonate ion (HCO_3^-) is itself an acid because it can release H^+ into solution. However, it also hydrolyzes:



By applying the Law of Mass Action to reaction 10.24 we have:

$$\frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} = K_{\text{H}_1} \quad (10.26)$$

and from equation 10.25:

$$\frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]} = K_{\text{H}_2} \quad (10.27)$$

To find the value of the first hydrolysis constant (K_{H_1}) we replace $[\text{OH}^-]$ in equation 10.26 by:

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \quad (10.28)$$

where K_w is the dissociation constant of water. Therefore, from equation 10.26:

$$\frac{[\text{HCO}_3^-]K_w}{[\text{CO}_3^{2-}][\text{H}^+]} = K_{\text{H}_1} \quad (10.29)$$

Since the dissociation of carbonic acid proceeds stepwise:



we see that in equation 10.29:

$$\frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}][\text{H}^+]} = \frac{1}{K_{\text{A}_2}} \quad (10.32)$$

By substituting equation 10.32 into equation 10.29 we obtain:

$$\frac{K_w}{K_{\text{A}_2}} = K_{\text{H}_1} \quad (10.33)$$

The same procedure yields:

$$\frac{K_w}{K_{\text{A}_1}} = K_{\text{H}_2} \quad (10.34)$$

from equation 10.27.

We are now able to calculate the pH of a solution that was prepared by dissolving 0.1 mol of

K_2CO_3 in one liter of pure water at 25°C. In addition, we specify that CO_2 gas does not escape from the solution. Since $K_{\text{A}_1} = 10^{-6.35}$ and $K_{\text{A}_2} = 10^{-10.3}$ (Table 9.3) and $K_w = 10^{-14}$, we find that $K_{\text{H}_1} = 10^{-3.7}$ and $K_{\text{H}_2} = 10^{-7.65}$. Since K_{H_1} is nearly 9000 times larger than K_{H_2} , the first reaction is much more productive than the second. We therefore attempt a stepwise solution. If x moles of the carbonate ion hydrolyze in the first step, we have at equilibrium:

$$[\text{CO}_3^{2-}] = 0.1 - x$$

$$[\text{HCO}_3^-] = [\text{OH}^-] = x$$

Substituting into equation 10.26 yields:

$$\frac{x^2}{0.1 - x} = 10^{-3.7} \quad (10.35)$$

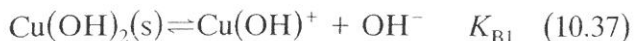
If $x \ll 0.1$, $0.1 - x \approx 0.1$ and, from equation 10.35, $x = 10^{-2.35}$, which is only 4.5% of 0.1. Therefore, the approximation that $x \ll 0.1$ is justified. The second hydrolysis step produces a negligible amount of additional hydroxyl ion equal to $[\text{OH}^-] = 10^{-7.65}$ mol/L. The pH of a solution obtained by dissolving 0.1 mole of K_2CO_3 in one liter of pure water at $T = 25^\circ\text{C}$ is:

$$\text{pH} = 14 - 2.35 = 11.65 \quad (10.36)$$

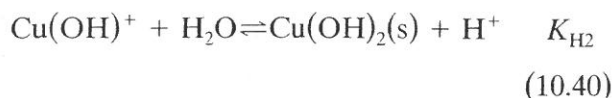
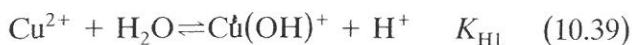
Clearly, the solution is quite basic, as predicted.

The problem can also be solved by means of a set of independent equations that arise from the simultaneous equilibria in the solution, from the requirement of electrical neutrality, and from the stipulation that the total amount of molecular and ionic carbonate species in the solution is 0.1 mol. We could have set ourselves a more general problem by allowing the solution to be open to the atmosphere, permitting the carbonate species in the solution to equilibrate with the CO_2 of the atmosphere. We choose not to do so here because we will treat carbonate equilibria in Section 10.4.

Salts derived from strong acids and *weak bases* also hydrolyze, and the necessary hydrolysis constants can be derived as demonstrated above. For example, $\text{Cu}(\text{OH})_2$ is a weak base that dissociates in two steps:

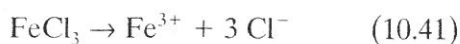


$\text{Cu}(\text{OH})_2$ forms the salt CuSO_4 by reaction with H_2SO_4 . When CuSO_4 is dissolved in water, Cu^{2+} is released and hydrolyzes, as shown:



where $K_{\text{H1}} = K_{\text{w}}/K_{\text{B2}}$ and $K_{\text{H2}} = K_{\text{w}}/K_{\text{B1}}$. Therefore, we predict that a solution of CuSO_4 in pure water becomes acidic because of the hydrolysis of the cupric ion (Cu^{2+}).

Hydrolysis is an important phenomenon because it enhances the solubility of salts formed from weak acids and bases and because it tends to stabilize the pH of salt solutions. Hydrolysis affects the solubility of salts by producing additional ionic and molecular species that permit more of the salt to dissolve. In fact, the solubility of salts derived from weak acids is greatly enhanced when they are dissolved in strong acids that provide an ample supply of hydrogen ions. Therefore, all carbonates, silicates, phosphates, and sulfides are more soluble in acids than in pure water because of the affinity of their anions for hydrogen ions. The same is true in principle of salts derived from weak bases, except that the bases they form may themselves be quite insoluble. For example, if we place ferric chloride into a basic solution, the Fe^{3+} ion reacts with OH^- to form insoluble $\text{Fe}(\text{OH})_3$:



Solutions that contain a weak acid and a salt of that acid are *buffered* because they resist changes in their pH. Consider, for example, a solution containing carbonic acid and K_2CO_3 . The carbonic acid is only partially dissociated, as indicated by equations 10.30 and 10.31. By adding K_2CO_3 , which releases additional CO_3^{2-} , the dissociation of the acid is even more inhibited and the concentration of molecular H_2CO_3

increases in accordance with Le Châtelier's principle. Therefore, the solution has effectively *stored* hydrogen ions, and they are released when a reaction occurs in this solution that consumes H^+ . Similarly, if additional hydrogen ions were to be released into the solution, they would be consumed by reacting with the carbonate and bicarbonate ions to form more carbonic acid.

10.3 Activities and Concentrations

We have assumed so far that the ions in electrolyte solutions do not interfere with each other. This can only be true in very dilute solutions because, in general, oppositely charged ions in a solution attract each other. Therefore, cations in an electrolyte solution are surrounded by anions and vice versa. The result is that the ions of a particular compound are less able to interact with each other than expected from their concentrations. We express this condition by saying that the *activity* of the ions in electrolyte solutions is *less* than their *concentration*. It is plausible to expect that the interference by the other ions increases with their concentrations and charges. Similarly, the effect of a given suite of ions on a particular ion depends on the charge of that ion and its radius, which together determine the charge density on the surface of the ion. In addition, the molecules of the solvent play a role because, if they have electrical polarity, they also interact with both anions and cations. All of these factors are included in the *Debye-Hückel theory*, on the basis on which the relationship between activity and concentration of ions in a solution of electrolytes can be estimated.

The concentrations and charges of ions in a solution are expressed by means of its *ionic strength*, defined as:

$$I = \frac{1}{2} \sum m_i z_i^2 \quad (10.43)$$

where m_i are the concentrations expressed in moles and z_i are the charges of the ions. The ionic strength of aqueous solutions on the surface of

the Earth generally ranges from about 1×10^{-3} in rivers and lakes to 1×10^{-1} in old groundwater. Seawater has an ionic strength of 7×10^{-1} and oilfield brines and brine lakes may have ionic strengths of 5 or more. In order to calculate the ionic strength of a water sample, we must have a complete chemical analysis, such as the analysis of water from the Mississippi River at New Orleans in Table 10.2. The concentrations of the ions are converted from parts per million (ppm) to moles per kilogram before they are entered into equation 10.43. The result is $I = 4.4 \times 10^{-3}$. Note that SiO_2 does not contribute to the ionic strength of this water because its charge is zero and that H^+ and OH^- are omitted because their concentrations are very low (about 10^{-7} mol/kg) unless the water is highly acidic or basic. Note also that the concentrations of H_2CO_3 and CO_3^{2-} were not reported in the analysis in Table 10.2 because HCO_3^{2-} is the dominant ion when the pH is between 6.35 and 10.3.

The ionic strength is used in the Debye-Hückel theory to estimate values of the activity coefficient γ defined by the equation:

$$[\text{activity}] = \gamma(\text{concentration}) \quad (10.44)$$

Table 10.2 Chemical Composition of Water of the Mississippi River at New Orleans

Ion	Concentration	
	ppm	mol/kg
HCO_3^-	116	1.90×10^{-3}
SO_4^{2-}	25.5	2.65×10^{-4}
Cl^-	10.3	2.90×10^{-4}
NO_3^-	2.7	4.3×10^{-5}
Ca^{2+}	34	8.5×10^{-4}
Mg^{2+}	8.9	3.7×10^{-4}
Na^+	11.9	5.17×10^{-4}
K^+	1.9 ^a	4.9×10^{-5}
Fe^{2+}	0.14	2.5×10^{-6}
SiO_2	11.7	1.95×10^{-4}

^aBased on $\text{Na}^+/\text{K}^+ = 6.4$ (concentration ratio) in average North American river water (Livingstone, 1963, Table 81, p. G41).

SOURCE: Livingstone (1963), Table 15, entry H, p. G15.

For dilute solutions having ionic strengths $< 5 \times 10^{-3}$ the relationship is, to good approximation:

$$-\log \gamma = Az^2I^{1/2} \quad (10.45)$$

where $A = 0.5085$ for water at 25°C , z is the charge of the ion whose activity coefficient is being calculated, and I is the ionic strength of the solution as defined by equation 10.43. Note that the activity coefficient of molecules is equal to one because their charge is equal to zero.

A more complete statement, valid for $I < 0.1$, is given by:

$$-\log \gamma = \frac{Az^2I^{1/2}}{1 + aBI^{1/2}} \quad (10.46)$$

where A and B are constants whose values depend on the dielectric constant of the solvent and the temperature, and a is the effective diameter of the ion in the solution in Ångstrom units. Values of A and B for water are listed in Table 10.3 as a function of temperature, and values of a of several ions in aqueous solution are compiled in Table 10.4. Equation 10.46 was used to calculate the activity

Table 10.3 List of Values for Constants Used in the Debye-Hückel Theory Expressed in Equation 10.46

Temperature, $^\circ\text{C}$	A	B
0	0.4883	0.3241
5	0.4921	0.3249
10	0.4960	0.3258
15	0.5000	0.3262
20	0.5042	0.3273
25	0.5085	0.3281
30	0.5130	0.3290
35	0.5175	0.3297
40	0.5221	0.3305
45	0.5271	0.3314
50	0.5319	0.3321
55	0.5371	0.3329
60	0.5425	0.3338

SOURCE: Garrels and Christ (1965).

Table 10.4 Values of Parameter a of Ions in Aqueous Solution

Ions	$a, \text{\AA}$
Rb ⁺ , Cs ⁺ , NH ₄ ⁺ , Tl ⁺ , Ag ⁺	2.5
K ⁺ , Cl ⁻ , Br ⁻ , I ⁻ , NO ₃ ⁻	3
OH ⁻ , F ⁻ , HS ⁻ , BrO ₃ ⁻ , IO ₄ ⁻ , MnO ₄ ⁻	3.5
Na ⁺ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , HSO ₃ ⁻ , Hg ₂ ²⁺ , SO ₄ ²⁻ , SeO ₄ ²⁻ , CrO ₄ ²⁻ , HPO ₄ ²⁻ , PO ₄ ³⁻	4.0–4.5
Sr ²⁺ , Ba ²⁺ , Ra ²⁺ , Cd ²⁺ , Hg ²⁺ , S ²⁻ , WO ₄ ²⁻	5.0
Li ⁺ , Ca ²⁺ , Cu ²⁺ , Zn ²⁺ , Sn ²⁺ , Mn ²⁺ , Fe ²⁺ , Ni ²⁺ , Co ²⁺	6
Mg ²⁺ , Be ²⁺	8
H ⁺ , Al ³⁺ , Cr ³⁺ , REE ³⁺	9
Th ⁴⁺ , Zr ⁴⁺ , Ce ⁴⁺ , Sn ⁴⁺	11

SOURCE: Garrels and Christ (1965).

coefficients for ions of different charges and hydrated radii shown in Figure 10.2. A third equation developed by Davies yields reliable results up to $I = 0.5$:

$$-\log \gamma = Az^2 \left[\frac{I^{1/2}}{1 + I^{1/2}} - 0.2I \right] \quad (10.47)$$

Further extensions of these methods by Pitzer (1973) enabled Harvie and Weare (1980) to calculate the solubilities of minerals in brines having ionic strengths greater than 20.

Activity coefficients for ions of different charges in solutions of varying ionic strengths, as determined from the Davies equation (10.47), are listed in Table 10.5. Note that the values of the activity coefficients in Table 10.5 *decrease* with increasing ionic strength of the solution and with increasing charge of the ion. For example, we find by interpolating in Table 10.5 that the activity of Na⁺ in water of the Mississippi River ($I = 4.4 \times 10^{-3}$) is about 0.936, whereas that of Ca²⁺ is 0.759, and that of La³⁺ is only 0.543. In other words, the presence of other ions reduces the effective concentration of Na⁺ in the Mississippi River by 6.4%, that of Ca²⁺ by 24.1%, and that of La³⁺ by 45.7%. In general, activity coefficients *decrease* with increasing ionic strength, but *increase* again at high values of I and may become larger than one (Garrels and Christ, 1965). The increase of the activity coefficient in highly saline

electrolyte solutions can be attributed to “crowding” of the ions, which counteracts the “interference” that occurs at lower ionic strengths.

The interference of other ions in the solution with the ions of a salt causes the solubility of the salt to increase. For example, the solubility of CaSO₄ in pure water at 25°C ($\gamma = 1.0$, $K_{sp} = 10^{-4.5}$) is $10^{-2.25}$ or 5.6×10^{-3} mol/L. However, in water of the Mississippi River ($I = 4.4 \times 10^{-3}$, $\gamma_{\pm 2} = 0.759$) the *concentration* of Ca²⁺ in equilibrium with anhydrite is:

$$(\text{Ca}^{2+}) = \frac{[\text{Ca}^{2+}]}{\gamma_{\pm 2}} = \frac{10^{-2.25}}{0.759} = 7.4 \times 10^{-3} \text{ mol/L} \quad (10.48)$$

which implies an *increase* of the solubility of anhydrite of 32.1%.

This result illustrates the point that the Law of Mass Action yields inaccurate results *unless* the concentrations of reactants and products of a reaction at equilibrium are converted to activities by means of activity coefficients in order to correct them for the nonideality of electrolyte solutions. Conversely, the results of calculations based on the Law of Mass Action are expressed in terms of *activities* and must be converted to concentrations before they are interpreted. The solubility calculation of anhydrite in Mississippi River water indicates that the presence of other ions in a solution must not be ignored.

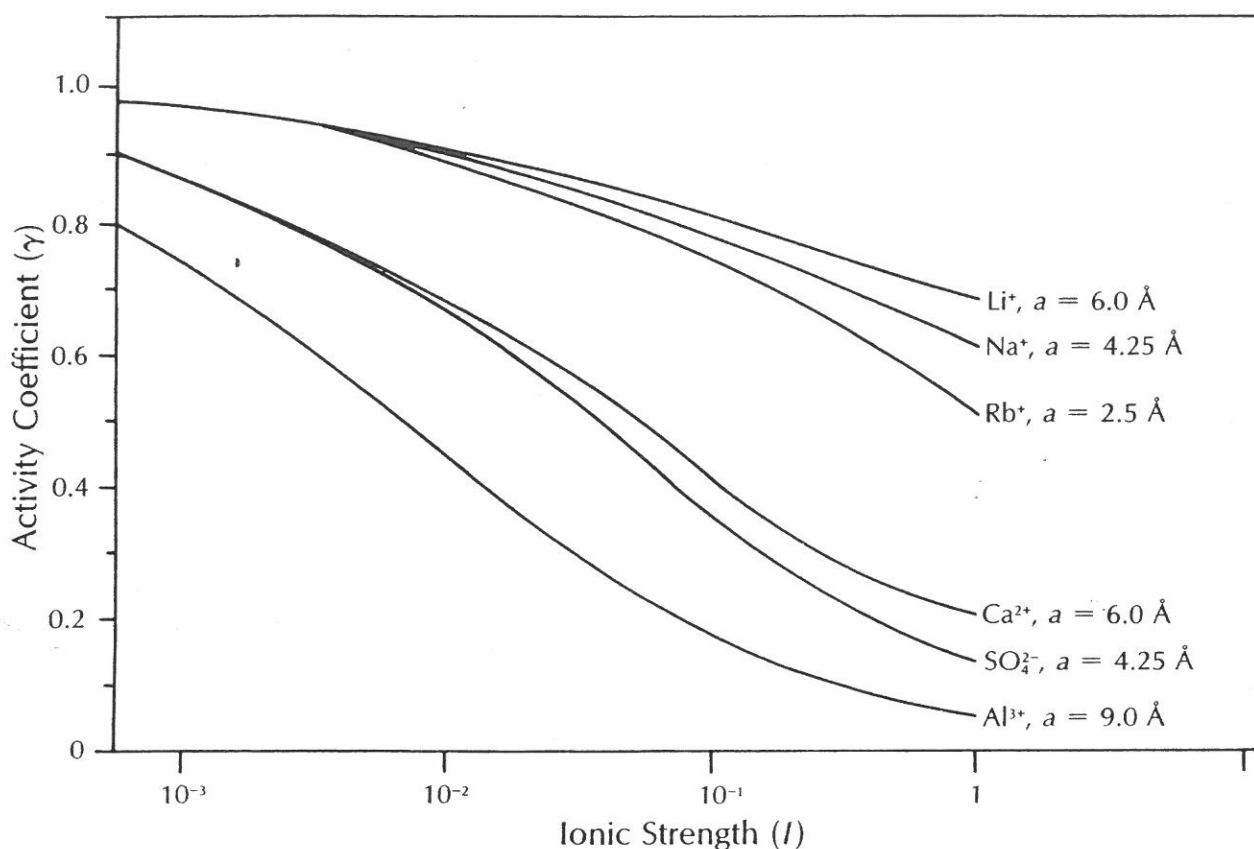


Figure 10.2 Variation of the activity coefficients of ions having different charges and hydrated radii with the ionic strength of aqueous solutions at 25°C. The curves were calculated from the Debye-Hückel theory expressed by equation 10.46 with data from Tables 10.3 and 10.4. Note that the magnitude of hydrated radii of ions of equal charge becomes important at $I > 10^{-2}$.

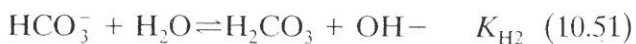
Table 10.5 Activity Coefficients for Ions of Different Charges in Electrolyte Solutions of Varying Ionic Strengths Based on Equation 10.47 by Davies

I	z		
	± 1	± 2	± 3
1×10^{-3}	0.97	0.87	0.73
5×10^{-3}	0.93	0.74	0.51
1×10^{-2}	0.90	0.66	0.40
5×10^{-2}	0.82	0.45	0.16
1×10^{-1}	0.78	0.36	0.10
2×10^{-1}	0.73	0.28	0.06
5×10^{-1}	0.69	0.23	0.04

SOURCE: Krauskopf (1979).

10.4 Solubility of Calcium Carbonate

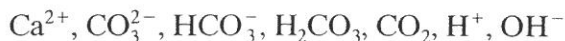
We are now ready to calculate the solubility of calcite, which is one of the most common minerals on the face of the Earth. The calculation requires all of the skills we have developed in applying the Law of Mass Action and is by no means trivial (Butler, 1982; Garrels and Christ, 1965). We start with the dissociation of calcite into ions at 25°C and the subsequent hydrolysis of the carbonate and bicarbonate ions to form carbonic acid:



If the solution is open to the atmosphere, carbonic acid is in equilibrium with carbon dioxide, which has a partial pressure of 3×10^{-4} atmosphere:



When calcite crystals are in equilibrium with their ions in pure water open to the atmosphere at 25°C, seven ions and molecules are present:



However, the partial pressure of CO_2 is fixed by the composition of the atmosphere, although soil gases may contain up to ten times as much CO_2 as the open atmosphere. Therefore, we need only six independent equations in order to specify the concentrations of all ions and molecules in a saturated solution of calcite. We obtain five equations by applying the Law of Mass Action to equations 10.49 through 10.52 and to the dissociation equilibrium of water. From equation 10.49:

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = 10^{-8.35} \quad (10.53)$$

From equations 10.50 and 10.51:

$$\frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} = K_{\text{H1}} = \frac{10^{-14.0}}{10^{-10.3}} = 10^{-3.7} \quad (10.54)$$

$$\frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]} = K_{\text{H2}} = \frac{10^{-14.0}}{10^{-6.35}} = 10^{-7.65} \quad (10.55)$$

Finally, from equation 10.52:

$$\frac{[\text{CO}_2]}{[\text{H}_2\text{CO}_3]} = 32.2 \quad (10.56)$$

and for water:

$$[\text{H}^+][\text{OH}^-] = 10^{-14.0} \quad (10.57)$$

The sixth equation arises from the requirement for electrical neutrality:

$$2(\text{Ca}^{2+}) + (\text{H}^+) = 2(\text{CO}_3^{2-}) + (\text{HCO}_3^-) + (\text{OH}^-) \quad (10.58)$$

We notice that according to equation 10.56:

$$\begin{aligned} [\text{H}_2\text{CO}_3] &= \frac{[\text{CO}_2]}{32.2} = \frac{3 \times 10^{-4}}{32.2} \\ &= 9.3 \times 10^{-6} \text{ mol/L} \end{aligned} \quad (10.59)$$

Evidently, the activity of carbonic acid is fixed by the partial pressure of CO_2 . We can use this result in equation 10.55 to express $[\text{HCO}_3^-]$ as a function of $[\text{OH}^-]$:

$$\begin{aligned} [\text{HCO}_3^-] &= \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{10^{-7.65}} \\ &= \frac{(9.3 \times 10^{-6})[\text{OH}^-]}{10^{-7.65}} \\ &= 10^{2.618}[\text{OH}^-] \end{aligned} \quad (10.60)$$

From equation 10.54 we derive a relationship between $[\text{CO}_3^{2-}]$ and $[\text{OH}^-]$:

$$\begin{aligned} [\text{CO}_3^{2-}] &= \frac{[\text{HCO}_3^-][\text{OH}^-]}{10^{-3.7}} = \frac{10^{2.618}[\text{OH}^-]^2}{10^{-3.7}} \\ &= 10^{6.318}[\text{OH}^-]^2 \end{aligned} \quad (10.61)$$

From equations 10.61 and 10.53 we obtain:

$$\begin{aligned} [\text{Ca}^{2+}] &= \frac{10^{-8.35}}{[\text{CO}_3^{2-}]} = \frac{10^{-8.35}}{10^{6.318}[\text{OH}^-]^2} \\ &= \frac{10^{-14.668}}{[\text{OH}^-]^2} \end{aligned} \quad (10.62)$$

Finally, from equation 10.57:

$$[\text{H}^+] = \frac{10^{-14.0}}{[\text{OH}^-]} \quad (10.63)$$

We now convert the activities of the ions to their corresponding concentrations for substitution into equation 10.58. In order to do so we must know the ionic strength of the solution, which depends on the concentrations of the ions it contains. Strictly speaking, we cannot determine the ionic strength without first completing the calculation. However, we cannot complete the calculation without knowing the ionic strength. We deal with this Catch-22 situation by *iteration*. That is, we assume that all activity coefficients are equal

to one, make the calculation, and then use the results to determine the ionic strength and hence the activity coefficients from the Davies equation (10.47) or from Table 10.5. We then return to equation 10.58, convert the activities of all ions to the appropriate concentrations, and solve the problem a second time. If necessary, the process can be repeated several times to achieve a desired level of accuracy.

Therefore, we now proceed with the solution of the problem by substituting equations 10.60, 10.61, 10.62, and 10.63 into equation 10.58, assuming that all activity coefficients are equal to one:

$$\frac{2 \times 10^{-14.668}}{[\text{OH}^-]^2} + \frac{10^{-14.0}}{[\text{OH}^-]} = (2 \times 10^{6.318})[\text{OH}^-]^2 + 10^{2.618}[\text{OH}^-] + [\text{OH}^-] \quad (10.64)$$

We simplify equation 10.64 by eliminating the term for (H^+) because the solution will be basic and by combining $10^{2.618}[\text{OH}^-] + [\text{OH}^-]$ as $10^{2.619}[\text{OH}^-]$. Next, we clear the fractions by multiplying all remaining terms by $[\text{OH}^-]^2$ and collect terms:

$$10^{6.619}[\text{OH}^-]^4 + 10^{2.619}[\text{OH}^-]^3 = 10^{-14.366} \quad (10.65)$$

Dividing each term by $10^{6.619}$ yields:

$$[\text{OH}^-]^4 + 10^{-4.000}[\text{OH}^-]^3 = 10^{-20.985} \quad (10.66)$$

We solve this equation by trial and error starting with $[\text{OH}^-] = 10^{-6.0}$ because we predict that the solution will be basic. Substituting into equation 10.66 yields $10^{-24} + 10^{-22}$, which is about 10 times smaller than $10^{-20.985}$. Therefore, $[\text{OH}^-]$ must be larger than $10^{-6.0}$. We note that $10^{-24} \ll 10^{-22}$ and therefore eliminate the first term from equation 10.66 to get:

$$10^{-4.000}[\text{OH}^-]^3 = 10^{-20.985} \quad (10.67)$$

which yields $[\text{OH}^-] = 10^{-5.66}$ mol/L. By substituting this value into equation 10.66 we find that the term we omitted is only 2.2% of $10^{-4.000}[\text{OH}^-]^3$, which is acceptable.

We can now calculate the activities of the other ions in the solution by substituting $[\text{OH}^-] = 10^{-5.66}$ into equations 10.60–10.63. The results are:

$$\begin{aligned} [\text{HCO}_3^-] &= 10^{2.618}[\text{OH}^-] = 10^{2.618} \times 10^{-5.66} \\ &= 10^{-3.042} = 9.08 \times 10^{-4} \text{ mol/L} \end{aligned}$$

$$\begin{aligned} [\text{CO}_3^{2-}] &= 10^{6.318}[\text{OH}^-]^2 = 10^{6.318} \times 10^{-11.32} \\ &= 10^{-5.002} = 9.95 \times 10^{-6} \text{ mol/L} \end{aligned}$$

$$\begin{aligned} [\text{Ca}^{2+}] &= \frac{10^{-14.668}}{[\text{OH}^-]^2} = \frac{10^{-14.668}}{10^{-11.32}} = 10^{-3.348} \\ &= 4.48 \times 10^{-4} \text{ mol/L} \end{aligned}$$

$$[\text{H}^+] = \frac{10^{-14.0}}{[\text{OH}^-]} = \frac{10^{-14.0}}{10^{-5.66}} = 10^{-8.34} \text{ mol/L}$$

We check the correctness of these results by calculating the IAP of calcite in this solution:

$$\text{IAP} = (9.95 \times 10^{-6}) \times (4.48 \times 10^{-4}) = 10^{-8.35} \quad (10.68)$$

which is identical to K_{sp} for calcite and therefore confirms the correctness of the calculation. The ionic strength of the solution is $I = 1.4 \times 10^{-3}$, and the activity coefficients of the ions from Table 10.5 are $\gamma_{\pm 1} = 0.966$ and $\gamma_{\pm 2} = 0.857$.

Returning to equations 10.60–10.63, we now convert the activities to concentrations:

$$\begin{aligned} (\text{HCO}_3^-) &= \frac{10^{2.618}[\text{OH}^-]}{\gamma_{\pm 1}} = \frac{10^{2.618}[\text{OH}^-]}{0.966} \\ &= 10^{2.633}[\text{OH}^-] \end{aligned}$$

$$\begin{aligned} (\text{CO}_3^{2-}) &= \frac{10^{6.318}[\text{OH}^-]^2}{\gamma_{\pm 2}} = \frac{10^{6.318}[\text{OH}^-]^2}{0.857} \\ &= 10^{6.385}[\text{OH}^-]^2 \end{aligned}$$

$$\begin{aligned} (\text{Ca}^{2+}) &= \frac{10^{-14.668}}{\gamma_{\pm 2}[\text{OH}^-]^2} = \frac{10^{-14.668}}{0.857[\text{OH}^-]^2} \\ &= \frac{10^{-14.600}}{[\text{OH}^-]^2} \end{aligned}$$

Substituting into equation 10.58, dropping (H^+), and combining the $[OH^-]$ terms as before, we obtain:

$$\frac{2 \times 10^{-14.600}}{[OH^-]^2} = (2 \times 10^{6.385})[OH^-]^2 + 10^{2.634}[OH^-] \quad (10.69)$$

Note that this equation is stated in terms of the *activities* of OH^- , which express the *concentrations* of the other ions. By solving equation 10.69 as before, we obtain $[OH^-] = 10^{-5.644}$ mol/L. This value yields for the other ions:

$$[HCO_3^-] = 9.42 \times 10^{-4} \text{ mol/L}$$

$$[CO_3^{2-}] = 1.07 \times 10^{-5} \text{ mol/L}$$

$$[Ca^{2+}] = 4.17 \times 10^{-4} \text{ mol/L}$$

$$[H^+] = 10^{-8.356} \quad \text{or} \quad \text{pH} = 8.36$$

The ionic strength, based on these results, is $I = 1.3 \times 10^{-3}$, which does not differ enough from the previous estimate to justify a repetition of the calculation. Therefore, the concentration of Ca^{2+} in the solution is:

$$(Ca^{2+}) = \frac{4.17 \times 10^{-4}}{0.857} = 4.86 \times 10^{-4} \text{ mol/L}$$

or 19.5 mg/L. The solubility (S) of calcite in water in equilibrium with CO_2 of the atmosphere at 25°C is:

$$S = 4.86 \times 10^{-4} \times 100.0787 = 4.86 \times 10^{-2} \text{ g/L}$$

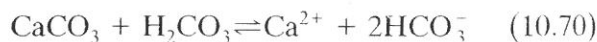
In addition, note that the pH of this solution is 8.36, thus confirming our prediction based on the effect of hydrolysis of the carbonate ion of calcite.

The chemical analysis in Table 10.2 indicates that the water in the Mississippi River has a Ca concentration of 34 ppm, which is nearly 75% larger than the value we obtained above. The difference is partly due to the higher ionic strength of water in the Mississippi River ($I = 4.4 \times 10^{-3}$) and to the correspondingly lower activity coefficients ($\gamma_{\pm 1} = 0.936$, $\gamma_{\pm 2} = 0.759$). However, allowance for the higher ionic strength increases

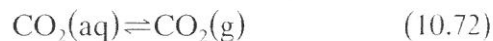
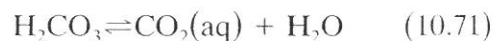
the predicted Ca concentration in the Mississippi River only to 22.0 mg/L and therefore does not resolve the discrepancy.

The water in the Mississippi River, like all natural solutions, contains a mixture of ions and molecules derived from different sources. Its Ca^{2+} content originates from the solution of calcium carbonate (calcite and aragonite), calcium sulfate (anhydrite and gypsum), and calcium phosphate (apatite) and from the transformation of plagioclase to kaolinite or other clay minerals. In addition, Ca^{2+} may be adsorbed on clay minerals and on the surfaces of other small mineral particles in suspension in the water. Finally, calcium occurs in many complex ions and molecules whose presence permits the calcium concentration of natural waters to exceed the concentration of Ca^{2+} based on the solubility of its principal minerals. A partial list of the complex ions of Ca includes $CaHCO_3^+$, $CaCO_3^0$, $CaCl^+$, $CaCl_2^0$, $CaNO_3^+$, $Ca(NO_3)_2^0$, $CaOH^+$, $Ca(OH)_2^0$, $CaPO_4^-$, $CaHPO_4^0$, $CaH_2PO_4^+$, $CaP_2O_7^{2-}$, $CaHP_2O_7^-$, $CaOHP_2O_7^{3-}$, $CaSO_4^0$ (Lindsay, 1979). The point is that natural waters are very complex and their compositions are not explainable by the solubility of a few common minerals. We therefore abandon the effort to explain the concentration of calcium or any other element in the Mississippi River. Instead, we use the discrepancy between the Ca^{2+} concentration of a saturated calcite solution and the calcium concentration in the water of the Mississippi River to consider how the solubility of calcite is affected by variations in the partial pressure CO_2 , the pH, and the temperature.

The reaction of calcite with carbonic acid between pH values of 6.35 and 10.3 can be represented by the equation:



where carbonic acid is also in equilibrium with aqueous CO_2 , which in turn is in equilibrium with CO_2 gas:



Note that equation 10.52 is the sum of 10.71 and 10.72 and that molecular CO_2 dissolved in water is thereby eliminated from consideration. We can use these equations to predict *qualitatively* how the solubility of calcite is affected by changes in the partial pressure of CO_2 . An *increase* in the partial pressure of CO_2 at constant temperature increases the concentration of carbonic acid in the solution. Consequently, more calcite *dissolves* by equation 10.70 in accordance with Le Châtelier's principle. Similarly, a *decrease* in the partial pressure of CO_2 causes a saturated solution of calcite to become supersaturated and results in the *precipitation* of calcite until equilibrium is restored.

The partial pressure of CO_2 at a site on the surface of the Earth may *decrease* as a result of photosynthesis of aquatic plants, which has the effect of combining CO_2 and H_2O to produce glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) and O_2 with the help of ultraviolet radiation. Consequently, communities of aquatic plants can lower the concentration of $\text{CO}_2(\text{aq})$ in the water during daylight hours. This may cause calcite to precipitate if the water becomes supersaturated with respect to calcite. Certain colonial algae are capable of precipitating calcite by this mechanism, thereby forming thinly laminated calcite mounds called *stromatolites* (Walter, 1977).

A similar process in limestone caverns results in the deposition of calcite *speleothems* in the form of *stalactites* and *stalagmites*. Limestone caverns form by the solution of calcite by water containing carbonic acid in accordance with equation 10.70. This process occurs primarily below the water table, and the solution cavities are initially filled with water. However, if the groundwater table is lowered because of uplift of the crust or a decrease in meteoric precipitation, the solution cavities above the water table become filled with air. Meteoric water percolating through the soil may equilibrate with CO_2 at a *higher* partial pressure than exists in the atmosphere and thus becomes a more effective solvent of calcite than it would have been had it equilibrated with CO_2 of the atmosphere. When this water forms a drop on the ceiling of a limestone cavern, the excess CO_2 escapes, the solution therefore may become supersaturated, and calcite may then precipitate

to form a *stalactite* hanging from the roof of the cavern. When the rate of flow of groundwater is so rapid that the solution does not reach equilibrium on the roof of the cavern, additional calcite may precipitate after the water has dripped onto the floor of the cavern, thereby forming a *stalagmite*. Ultimately, stalactites and stalagmites may join to become pillars or curtains of calcite.

The effect of the partial pressure of CO_2 on the solubility of calcite is shown quantitatively in Figure 10.3. Here we see that the concentration of Ca^{2+} in a saturated solution of calcite at 25°C increases from about 20 mg/L to about 45 mg/L when the partial pressure of CO_2 increases from 3×10^{-4} atm in the air to 3×10^{-3} atm in soil gases. Consequently, each liter of water appearing on the roof of a cavern could, under ideal conditions, deposit 25 mg of calcite. The amount of calcite that is actually deposited depends on the partial pressure of CO_2 in the soil above a given cavern, on the temperature, and on the establishment of equilibrium between calcite and the groundwater before the water reaches the cavern. Nevertheless, stalactites and stalagmites can grow

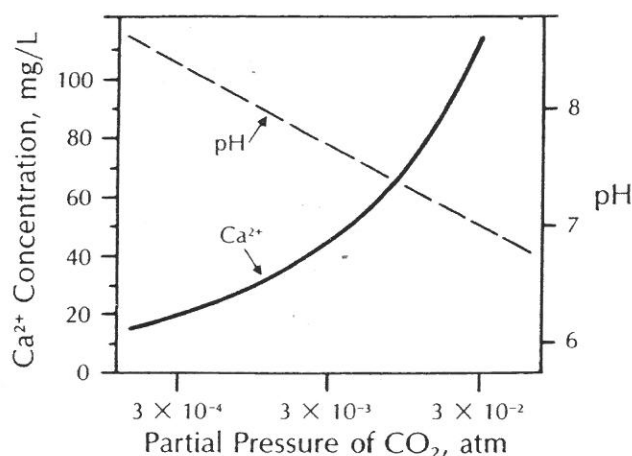


Figure 10.3 Increase of the solubility of calcite in water at 25°C with increasing partial pressure of CO_2 from 3×10^{-4} to 3×10^{-2} atm. The solubility of calcite is expressed as the concentration of Ca^{2+} in a saturated solution based on ionic strengths, which rise from 1.3×10^{-3} to 6.3×10^{-3} , whereas the pH decreases, as more CO_2 dissolves.

to large size over thousands or tens of thousands of years.

The solubility of calcite increases very significantly with increasing acidity of the solution, if the pH is controlled independent of the carbonate equilibria. Equation 10.62 provides a relationship between the activity of Ca^{2+} in a saturated solution of calcite in equilibrium with CO_2 of the atmosphere of 25°C and the activity of OH^- . Replacing $[\text{OH}^-]$ by $K_w/[\text{H}^+]$ gives:

$$[\text{Ca}^{2+}] = \frac{10^{-14.668}}{[\text{OH}^-]^2} = \frac{10^{-14.668}[\text{H}^+]^2}{(K_w)^2} \quad (10.73)$$

$$= 10^{13.332}[\text{H}^+]^2$$

Taking logarithms of both sides and converting $[\text{H}^+]$ to pH, we obtain:

$$\log [\text{Ca}^{2+}] = 13.332 - 2\text{pH} \quad (10.74)$$

This equation indicates that the solubility of calcite changes by a factor of 100 when the pH is varied by one unit. For example, at $\text{pH} = 7$, $[\text{Ca}^{2+}] = 2.15 \times 10^{-1}$ mol/L, whereas at $\text{pH} = 6$, $[\text{Ca}^{2+}] = 2.15 \times 10^{-3}$ mol/L. Evidently, when calcite reacts with an excess amount of a strong acid, its solubility is very high. Similarly, calcite cannot persist as a stable phase in natural environments that are even mildly acidic. For example, calcite in till of Wisconsin age in the midcontinent area of North America has been removed by leaching to depths of about one meter or more in only 15,000 years.

The solubility of calcite is also affected by the temperature because of changes in the numerical values of all of the equilibrium constants. Garrels and Christ (1965) compiled the set of values of the relevant equilibrium constants between 0 and 50°C that is listed in Table 10.6. We see by inspection that the dissociation constants of carbonic acid *increase* with increasing temperature, whereas the solubility product constants of calcite and CO_2 *decrease*. As a result, the solubility of calcite in pure water in equilibrium with CO_2 of the atmosphere actually *decreases* with increasing temperature, as shown in Figure 10.4. For example, a saturated solution of calcite in equilibrium with CO_2 at 3×10^{-3} atm contains about 75 mg/L

of Ca^{2+} at 5°C but only 40 mg/L at 30°C . Such changes in the environmental conditions may occur when cold water from the bottom of the oceans rises to the surface and is warmed in a shallow lagoon. As a result, seawater may become supersaturated with respect to calcite (or aragonite) because of the *increase* in temperature as well as the *decrease* in the partial pressure of CO_2 . However, carbonate sediment in the oceans is primarily of biogenic origin and results from the secretion of carbonate skeletons by plants and animals living in the water.

The opposite environmental changes are experienced by skeletal carbonate grains sinking through the ocean toward the bottom. Oceanic bottom water is colder than surface water and contains more dissolved CO_2 produced by decay of organic material. Consequently, the solubility of calcite (or aragonite) rises with increasing depth, and skeletal carbonate particles dissolve as they sink in the oceans. Whether such particles survive the trip through the water column and reach the bottom of the oceans depends on the

Table 10.6 Equilibrium Constants of Carbonate Equilibria as a Function of Temperature^a

Temperature, °C	$\text{p}K_{\text{A1}}$	$\text{p}K_{\text{A2}}$	$\text{p}K_{\text{sp}}$	$\text{p}K_{\text{CO}_2}$
0	6.58	10.62	8.02	1.12
5	6.52	10.56	8.09	(1.21) ^b
10	6.47	10.49	8.15	(1.28)
15	6.42	10.43	8.22	(1.35)
20	6.38	10.38	8.28	(1.41)
25	6.35	10.33	8.34	1.47
30	6.33	10.29	8.40	(1.52)
40	6.30	10.22	8.52	1.64
50	6.29	10.17	8.63	(1.74)

^a $\text{p}K_{\text{A1}} = -\log K_{\text{A1}}$; $\text{p}K_{\text{A2}} = -\log K_{\text{A2}}$; $\text{p}K_{\text{sp}} = -\log K_{\text{sp}}$; $\text{p}K_{\text{CO}_2} = -\log K_{\text{CO}_2}$ for $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$

^bValues in parentheses were obtained by graphical interpolation.

SOURCE: Garrels and Christ (1965), Table 3.2.

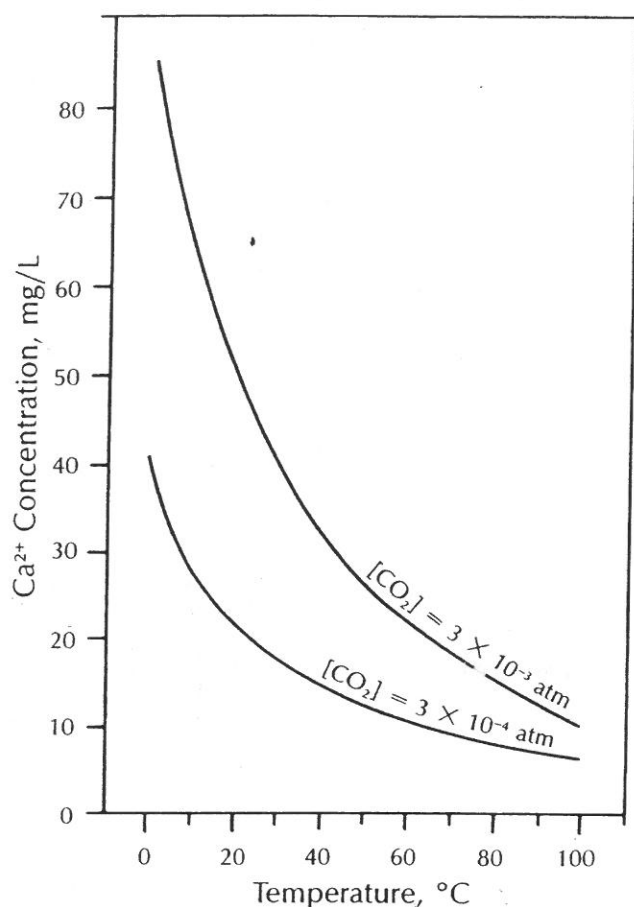


Figure 10.4 Decrease of the concentration of Ca^{2+} in a saturated solution of calcite in pure water with increasing temperature at two partial pressures of CO_2 . Activity coefficients were taken from Table 10.5 for the ionic strengths of the solutions, which range from about 5×10^{-3} ($P_{CO_2} = 3 \times 10^{-3}$ atm, $5^\circ C$) to 0.5×10^{-3} ($P_{CO_2} = 3 \times 10^{-4}$ atm, $80^\circ C$).

rates at which they sink and dissolve. If the water is deep enough, carbonate particles dissolve before they reach the bottom. Therefore, no carbonate sediment can accumulate in the oceans below this critical depth, which is known as the *carbonate compensation depth* (CCD).

10.5 Chemical Weathering

The solution of calcite as limestone or as mineral grains in soil is a form of chemical weathering. The chemical reactions that take place in this case

are the dissociation of the compound into ions as it dissolves in the water, accompanied by hydrolysis of the carbonate ion. The point here is that calcite and many other naturally occurring chemical compounds dissolve *congruently*, that is, without forming another compound. However, the Al silicate minerals generally dissolve *incongruently*; that is, they react with water to form another solid compound as well as ions and molecules.

The process of chemical weathering not only includes the congruent and incongruent solution of minerals but also encompasses all kinds of interactions of water and atmospheric gases with minerals at or near the surface of the Earth. Chemical weathering also includes oxidation-reduction reactions, which we will take up in Chapter 14. The reactions that constitute chemical weathering are not restricted to the surface of the Earth where minerals are actually exposed to the weather, but also operate effectively in soils and below the groundwater table where minerals are continuously in contact with water. The products of chemical weathering consist of (1) new minerals such as clay minerals, oxides, and hydroxides; (2) ions and molecules that dissolve in the water; and (3) grains of minerals that are unreactive such as quartz, garnet, zircon, muscovite, and native gold.

The solid weathering products, including new compounds and resistant minerals, are a major source of "sediment" that may accumulate in residual deposits at the site of weathering or is transported to the oceans where it is deposited and ultimately forms clastic sedimentary rocks. The ions and molecules in solution determine the chemical composition or "quality" of water and make up the solution load that is transported to the oceans by streams. Ultimately, as noted in Chapter 4, these ions and molecules are removed from the oceans by precipitation of compounds or by adsorption on solid particles. Evidently, chemical weathering is part of the *geochemical machine* that operates on the surface of the Earth. Chemical and mechanical forms of weathering cause the destruction of rocks, thereby releasing the elements for a trip to the ocean. We recognize, of course, that the trip to the ocean may be delayed by deposition of sediment or of dissolved constituents in basins on the continents and

that chemical weathering occurs also in the oceans themselves. Some of these complexities will become the subject of more detailed consideration in Part V of this book. For the time being, we attempt to apply the Law of Mass Action to the chemical weathering of a common Al silicate such as K-feldspar.

10.6 Transformation of Potassium Feldspar to Kaolinite

When K-feldspar (orthoclase or microcline) in igneous or high-grade metamorphic rocks is exposed to chemical weathering, it develops a "chalky" appearance caused by the formation of *kaolinite*. This mineral belongs to the large group of clay minerals (Chapter 13) that can form by chemical weathering of Al-silicate minerals of igneous and metamorphic rocks, by reactions involving volcanic glass, by hydrothermal processes, and by transformations from other clay minerals. In order to apply the Law of Mass Action to the reaction that causes K-feldspar to form kaolinite, we must first write the equation that represents this reaction. The construction of such equations requires an understanding of the chemical properties of the elements that may participate in the reaction and of the environment in which the reaction takes place. Therefore, we set up a list of guidelines that will govern the way in which we construct equations for chemical reactions in nature.

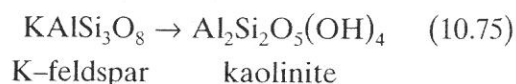
We start by placing the reactant on the left and the known product on the right side of the equation and then proceed to balance the equation based on the following conventions and requirements, provided that the valence numbers of the elements do *not* change during the reaction.

1. In reactions involving Al-silicates the Al is conserved; that is, it does not dissolve appreciably but is transferred into the solid product of the reaction.
2. Excess Si forms silicic acid, which does not dissociate unless the environment is very basic ($\text{pH} > 9.0$).
3. Alkali metals and alkaline earth elements form ions in solution.

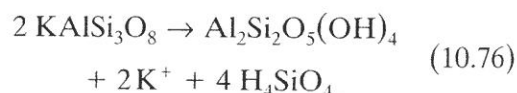
4. Any H^+ ions consumed by the reaction originate from the environment.
5. After the equation has first been balanced with respect to Al, Si, and soluble cations, we balance oxygen by adding H_2O as necessary.
6. We then balance hydrogen by adding H^+ as needed.
7. The equation must be balanced both in terms of matter and in terms of electrical charges.

Note that oxygen cannot be balanced by O_2 unless the reaction involves oxidation-reduction. In balancing oxidation-reduction reactions the electrons that are exchanged must be balanced first before a balance of matter and electrical charges is accomplished.

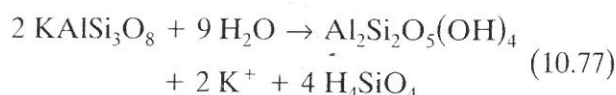
The rules listed above now permit us to construct an equation for the conversion of K-feldspar to kaolinite. We start by writing down the known reactant and its product:



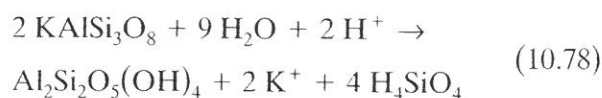
Next, we balance Al and then take care of K and Si:



We now have 16 oxygens on the left and $9 + 16 = 25$ oxygens on the right. Therefore, we add 9 H_2O to the left side of the equation to balance oxygen:



Finally, we have 18 hydrogens on the left and $4 + 16 = 20$ hydrogens on the right. Therefore, equation 10.77 is balanced in all respects by adding two H^+ to the left side:



This equation also satisfies the requirement for electrical neutrality because we have two positive charges on the left and two on the right side.

We now examine the equation we have constructed to learn by the application of Le Châtelier's principle how the reaction at equilibrium responds to changes in certain environmental parameters. We recall that reactions in nature may not achieve equilibrium but run to completion if one of the products escapes from the system. In the case we are considering, this could occur if K^+ and H_4SiO_4 are removed by the movement of the water in which the reaction is taking place. Therefore, the conversion of K-feldspar to kaolinite is favored by the movement of groundwater or surface water in response to a hydraulic or topographic gradient. We also note that nine moles of water are consumed for each mole of kaolinite that is produced. Therefore, the formation of kaolinite is favored by an abundance of water, which, in addition, must be acidic to provide the H^+ needed by the reaction. We conclude, therefore, that K-feldspar is converted into kaolinite in places where an abundance of acidified water is available and where the water flows at a sufficient rate to remove the soluble products of the reaction. Also, since reaction rates generally double for every $10^\circ C$ increase in temperature, the formation of kaolinite is likely to be favored by tropical climatic conditions near the equator of the Earth.

The reaction between K-feldspar and water involves the hydrolysis of a salt derived from a weak acid and strong base. We predict that such a reaction should remove H^+ from the solution and increase its pH. This is indeed the case here because H^+ is consumed by the reaction. However, the predicted increase of the pH can only be demonstrated in the laboratory because natural waters are buffered (Wollast, 1967). Therefore, when this reaction occurs in nature, the H^+ originates from the environment by the dissociation of carbonic or hydrosulfuric acid, or some other reaction. If the supply of H^+ is large and if the soluble products are removed, the reaction can run to completion. If, however, the water is basic and the soluble products remain at the site, the reaction can achieve equilibrium. In that case, the conversion of K-feldspar to kaolinite stops and the reaction becomes unproductive. Therefore, the establishment of chemical equilibrium may *prevent* the formation of a poten-

tially valuable mineral deposit and, in that sense, is not desirable from our point of view.

The probability that a chemical reaction in nature, such as equation 10.78, can achieve equilibrium depends, among other things, on the water/rock ratio. If there is an abundance of water compared to the volume of rock, reactions are likely to run to *completion* because the environment controls the reaction. If, on the other hand, the water/rock ratio is small, the reactions control the environment and *equilibrium* is possible, provided reaction rates are adequate. Therefore, reactions taking place in large bodies of water and in aquifers with high percolation rates having large water/rock ratios are more likely to run to completion than to achieve equilibrium, whereas reactions in small volumes of pore water (small water/rock ratios) may achieve a localized state of equilibrium between ions and their solids. Such restricted environments occur in the pore spaces of rocks in which mineral cements may be deposited by reactions that maintain a state of equilibrium.

The Law of Mass Action enables us to determine the activities of ions and molecules required for equilibrium in a chemical reaction represented by a balanced equation. Therefore, we return to equation 10.78 and place that reaction at equilibrium. By applying the Law of Mass Action we obtain:

$$\frac{[H_4SiO_4]^4[K^+]^2}{[H^+]^2} = K \quad (10.79)$$

We "linearize" this equation by taking logarithms:

$$4 \log[H_4SiO_4] + 2 \log[K^+] - 2 \log[H^+] = \log K \quad (10.80)$$

In order to reduce the number of variables to two, we combine K^+ and H^+ as the $[K^+]/[H^+]$ ratio:

$$4 \log[H_4SiO_4] + 2 \log \frac{[K^+]}{[H^+]} = \log K \quad (10.81)$$

We rewrite this equation as:

$$\log \frac{[K^+]}{[H^+]} = \frac{1}{2} \log K - 2 \log[H_4SiO_4] \quad (10.82)$$

which is the equation of a straight line in coordinates of $\log [K^+]/[H^+]$ and $\log [H_4SiO_4]$ having a

slope $m = -2$ and an intercept of $b = \frac{1}{2} \log K$. It is the locus of all points whose coordinates are the logarithms of the $[K^+]/[H^+]$ ratio and of $[H_4SiO_4]$ required for equilibrium of reaction 10.78. Thus, any point P on the line in Figure 10.5 (equation 10.82) represents an environment in which K-feldspar and kaolinite coexist in equilibrium with the ions and molecules in equation 10.78. Further, any point that is *not* on the line represents an environment in which K-feldspar and kaolinite are *not* at equilibrium. In that case, the reaction

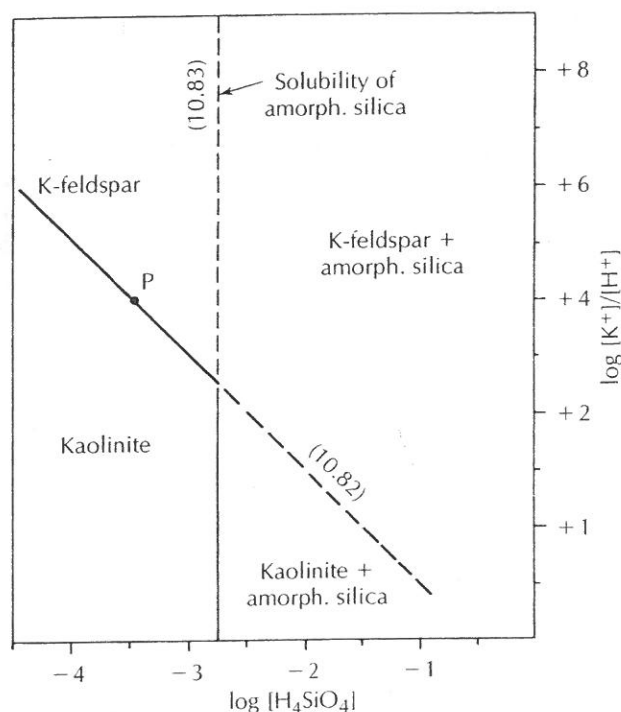
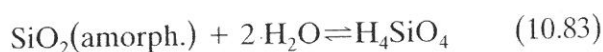


Figure 10.5 Partially completed activity diagram depicting the environmental conditions required to convert K-feldspar into kaolinite, and vice versa, in the presence of water at 25°C. The line labeled 10.82 represents conditions at which K-feldspar and kaolinite coexist in equilibrium. Point P on the line was chosen arbitrarily to help determine the direction of reaction 10.78 when $[H_4SiO_4]$ is increased or decreased. Line 10.83 represents the solubility of amorphous silica, which limits the activity of $[H_4SiO_4]$ to values less than $10^{-2.74}$ mol/L, as shown in equation 9.89. (Line 10.82 was plotted from equation 10.16 of Garrels and Christ, 1965.)

will proceed in the direction that moves it closer to a state of equilibrium. If the water/rock ratio is small, the environmental parameters can change until they satisfy equation 10.82 and equilibrium is established. If the water/rock ratio is large, the environmental parameters may not be affected appreciably by the reaction we are now considering. The reaction therefore runs to completion and does *not* achieve equilibrium.

The straight line we have drawn in Figure 10.5 (equation 10.82) is a boundary that separates the environments in which K-feldspar is produced by reaction 10.78 from those in which kaolinite is produced. We assume here that the reaction represented by equation 10.78 is, in fact, reversible. Although this may not be true in all cases, a K-feldspar known as *adularia* does form from kaolinite at low temperature (Mensing and Faure, 1983; Kastner and Siever, 1979). In any case, if we move from point P on the equilibrium line in Figure 10.5 toward higher activities of H_4SiO_4 , the reaction will respond by combining kaolinite with H_4SiO_4 to produce K-feldspar. Therefore, K-feldspar is the stable phase in all environments represented in Figure 10.5 that have an excess of H_4SiO_4 above that required for equilibrium. Similarly, kaolinite is stable in all environments containing less H_4SiO_4 than is required for equilibrium of reaction 10.78.

The activity of silicic acid is limited by its solubility, as shown in Figure 9.4. Therefore, amorphous silica precipitates when its solubility limit is reached and the activity of $[H_4SiO_4]$ in Figure 10.5 cannot rise above the value required for equilibrium in the reaction:



At equilibrium, $[H_4SiO_4] = 10^{-2.74}$ mol/L (equation 9.89). Therefore, a line has been drawn in Figure 10.5 at $\log [H_4SiO_4] = -2.74$ which is an impenetrable boundary because $[H_4SiO_4]$ cannot rise to higher values. The two lines in Figure 10.5, therefore, divide the compositional plane into three fields that represent environmental conditions needed to stabilize K-feldspar, kaolinite, and amorphous silica.

The procedure we have used to determine the environmental conditions necessary for the conversion of K-feldspar to kaolinite can serve to define the stabilities of all minerals that may be exposed to water and atmospheric gases at or near the surface of the Earth. Unfortunately, we cannot proceed in this direction because the equilibrium constants of the reactions we want to study have not been measured owing to experimental difficulties. For this reason, we next undertake a brief excursion into thermodynamics because it is possible to calculate equilibrium constants for chemical reactions from the change in the standard free energy of reactants and products. Thermodynamics will enable us to evaluate most chemical reactions we may care to investigate and will also provide a proof for the validity of the Law of Mass Action.

10.7 Summary

When salts dissolve in water, they dissociate into cations and anions. The solubility of a salt can be determined by calculating the activities of its ions in a saturated solution based on the Law of Mass Action. A salt may precipitate from a supersaturated solution in which the ion activity product (IAP) of its ions exceeds its solubility product constant. When a salt does precipitate, the concentration of its ions remaining in the solution change and their ratio tends toward infinity or zero. The resulting change in the chemical composition of the water contributes to the evolution of brines formed by progressive evaporation of water in desert lakes or in sediment drying in the sun.

The precipitation of salt A may also be caused by the addition of another, more soluble, salt B that shares a common ion with salt A. As a result, salt A precipitates as salt B dissolves until equilibrium between the ions and both salts is established. This process can account for the replacement of a mineral (salt B) by another (salt A) that is less soluble.

Salts can be classified on the basis of the strength or weakness of the acids and bases from which they originated. When the ions of a weak acid or weak base are released into solution by the dissociation of a salt, they react with water to

form the parental weak acid or weak base. This phenomenon is called hydrolysis and causes the pH of a salt solution to change. Hydrolysis of carbonates, silicates, and phosphates of the alkali metals and alkaline earths tends to make ground-water basic, thereby enhancing their solubility. In addition, salt solutions that also contain the parental acid (or base) of the salt resist change in their pH and are therefore said to be buffered.

The ability of the ions of a salt in solution to interact with each other is diminished by the presence of other ions and by interactions with the molecules of the solvent. Therefore, the molar concentrations of ions must be corrected by factors called activity coefficients derived from the Debye-Hückel theory before they are used in applications of the Law of Mass Action. Similarly, calculations based on the Law of Mass Action yield the activities of ions, which must then be converted to concentrations before they can be compared with observed concentrations determined by chemical analyses.

The solubility of calcium carbonate is enhanced by the hydrolysis of the carbonate ion and also rises with increasing partial pressure of CO_2 , with decreasing pH of the environment, and decreasing temperature. These relationships are all derivable by applications of the Law of Mass Action and explain such diverse phenomena as the deposition of stromatolites, the formation of limestone caverns, the growth of stalactites and stalagmites, leaching or deposition of calcium carbonate in soils, and the existence of the carbonate compensation depth (CCD) in the oceans.

The Law of Mass Action can also be used to study chemical weathering of Al silicates such as K-feldspar, which is converted by incongruent solution into kaolinite. These kinds of reactions can be represented by equations that are constructed on the basis of certain assumptions and conventions. The equations indicate the necessary conditions for the complete conversion of one mineral into another, although the decomposition of Al silicates is not reversible at surface temperatures in many cases. The equations also yield the activities of ions and mole-

cules required for equilibrium and thereby define the stability limits of the solids. By plotting the relevant equations derived from the Law of Mass Action in log-log coordinates, useful diagrams can be constructed that depict the

environmental conditions at which the solids are stable. The numerical values of the equilibrium constants required for this purpose can be calculated from thermodynamics, which is the topic of the next chapter.

Problems

1. Calculate activities of Ca^{2+} and F^- and the solubility of fluorite (CaF_2) in pure water at 25°C without regard to possible hydrolysis. Assume that all activity coefficients are equal to one. Express the solubility of fluorite in terms of mol/L and g/100 mL.

2. A quantity of 0.50 g of crystalline NaCl is added to one liter of a solution containing $10^{-3.0}$ mol of dissolved Ag^+ . Demonstrate that AgCl precipitates from the solution and calculate the weight of AgCl in grams that forms per liter. Assume that all activity coefficients are equal to one.

3. What is the ratio of the activities of Zn^{2+} and Pb^{2+} in a solution that is in equilibrium with respect to sphalerite (ZnS) and galena (PbS)? (Disregard hydrolysis effects.)

4. Predict the outcome of reactions that occur when a solution having $[\text{Cu}^{2+}]/[\text{Fe}^{2+}] = 10$ comes in contact with hydrotroilite (FeS). What will be the ratio of $[\text{Cu}^{2+}]/[\text{Fe}^{2+}]$ in the solution after equilibrium is established? (Disregard hydrolysis effects.)

5. Calculate the ionic strengths of water in Lake Superior (A) and Lake Erie (B) and explain the difference (Livingstone, 1963, Table 7). The concentrations are in mg/L.

	A	B
HCO_3^-	50.0	121
SO_4^{2-}	4.8	28
Cl^-	1.5	17

NO_3^-	0.52	1.2
Ca^{2+}	14.1	39
Mg^{2+}	3.7	8.7
Na^+	2.9	8.2
K^+	0.5	1.4
Fe^{2+}	0.36	0.03
SiO_2	4.1	2.1

6. Calculate the activity coefficient of Mg^{2+} in an aqueous solution having $I = 5 \times 10^{-2}$ at 15°C based on the Debye-Hückel theory represented by equation 10.46.

7. Calculate the solubility of strontianite (SrCO_3) in pure water at 25°C in equilibrium with CO_2 having a partial pressure of 3×10^{-4} atm. Specify the concentrations of all ions in a saturated solution in units of mol/L.

8. Calculate the solubility of calcite at 15°C in pure water in equilibrium with CO_2 at 3×10^{-3} atm pressure. Set up the equations based on the dissociation of carbonic acid and solve for the activity of H^+ . Specify the concentrations of all ions and express (Ca^{2+}) in mg/L.

9. Construct an equation to represent the incongruent solution of K-feldspar (KAlSi_3O_8) to "illite" ($\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$).

References

- BUTLER, J. N., 1982. *Carbon Dioxide Equilibria and Their Applications*. Addison-Wesley, Reading, MA, 259 pp.
- GARRELS, R. M., and C. L. CHRIST, 1965. *Solutions, Minerals and Equilibria*. Harper & Row, New York, 450 pp.
- HARDIE, L. A., and H. P. EUGSTER, 1970. The evolution of closed-basin brines. *Mineral. Soc. Amer. Spec. Pub.* 3, 273-290.
- HARVIE, C. E., and J. H. WEARE, 1980. The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO₄-

- H₂O system from zero to high concentration at 25°C. *Geochim. Cosmochim. Acta*, **44**:981-997.
- KASTNER, M., and R. SIEVER, 1979. Low temperature feldspars in sedimentary rocks. *Amer. J. Sci.*, **279**:435-479.
- KRAUSKOPF, K. B., 1979. *Introduction to Geochemistry*, 2nd ed. McGraw-Hill, New York, 617 pp.
- LINDSAY, W. L., 1979. *Chemical Equilibria in Soils*. Wiley, New York, 449 pp.
- LIVINSTONE, D. A., 1963. Chemical composition of rivers and lakes. In M. Fleischer (Ed.), *Data of Geochemistry*, 6th ed. Ch. G., *U.S. Geol. Surv. Prof. Paper* 440-G, 64 pp.
- MENSING, T. M., and G. FAURE, 1983. Identification and age of neoformed Paleozoic feldspar (adularia) in a Precambrian basement core from Scioto County, Ohio, USA. *Contrib. Mineral. Petrol.*, **82**:327-333.
- PITZER, K. S., 1973. Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.*, **77**:268-277.
- WALTER, M. R., 1977. *Stromatolites*. Elsevier, Amsterdam, 790 pp.
- WEAST, R. C., M. J. ASTLE, and W. H. BEYER (Eds.), 1986. *CRC Handbook of Chemistry and Physics*, 66th ed. CRC Press, Boca Raton, FL.
- WOLLAST, R., 1967. Kinetics of the alteration of K-feldspar in buffered solutions at low temperature. *Geochim. Cosmochim. Acta*, **31**:635-648.