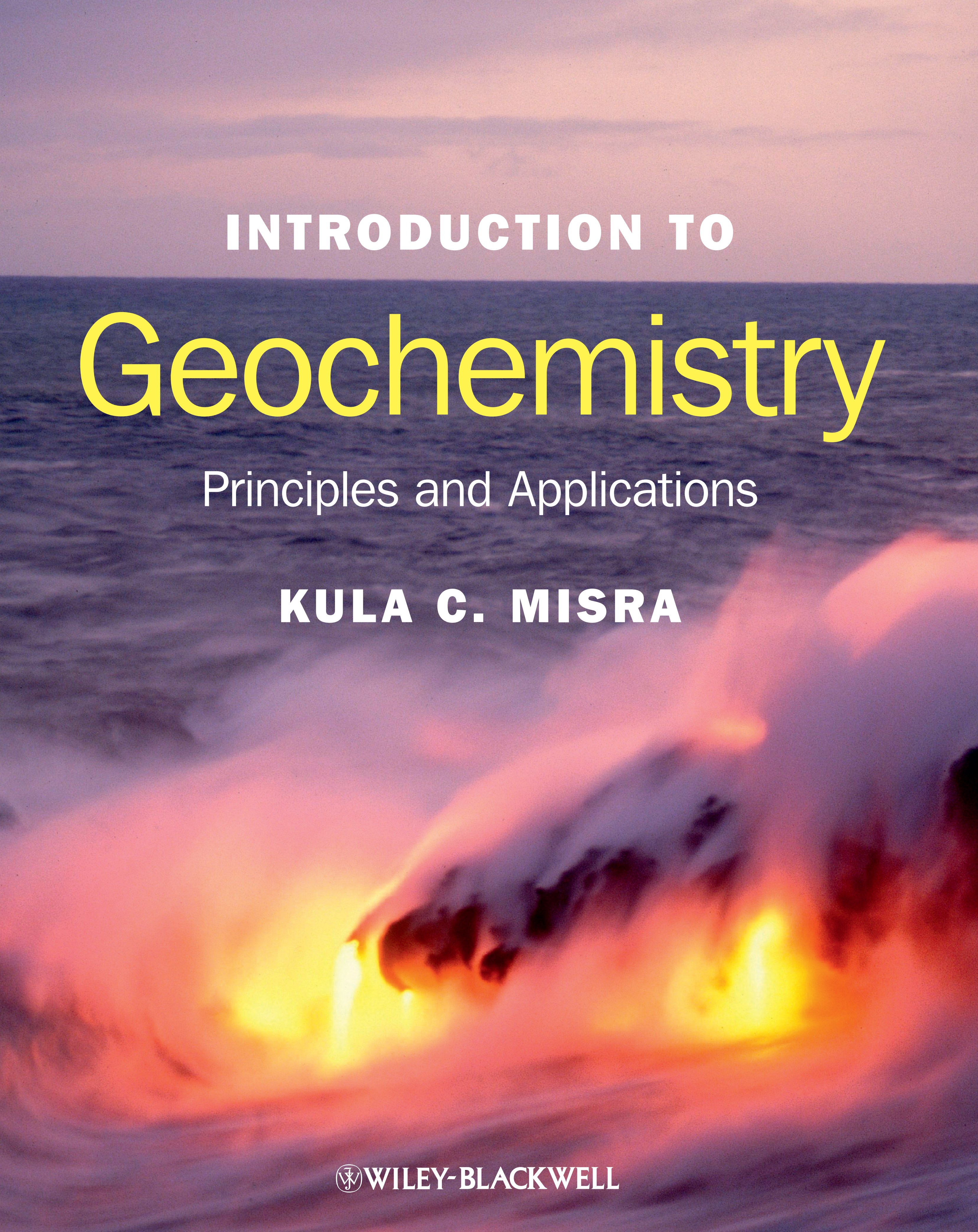

INTRODUCTION TO

Geochemistry

Principles and Applications

KULA C. MISRA

WILEY-BLACKWELL

ATOMIC WEIGHTS OF THE ELEMENTS

Element	*Symbol*	*Atomic Number*	*Atomic Weight*	*Element*	*Symbol*	*Atomic Number*	*Atomic Weight*
Actinium	Ac	89	r	Mercury	Hg	80	200.59
Aluminum	Al	13	26.98	Molybdenum	Mo	42	95.94
Americium	Am	95	r	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.76	Neon	Ne	10	20.18
Argon	Ar	18	39.95	Neptunium	Np	93	r
Arsenic	As	33	74.92	Nickel	Ni	28	58.69
Astatine	At	85	r	Niobium	Nb	41	92.91
Barium	Ba	56	137.33	Nitrogen	N	7	14.01
Berkelium	Bk	97	r	Nobelium	No	102	259.10
Beryllium	Be	4	9.01	Osmium	Os	76	190.23
Bismuth	Bi	83	208.98	Oxygen	O	8	16.00
Boron	B	5	10.81	Palladium	Pd	46	106.40
Bromine	Br	35	79.90	Phosphorus	P	15	30.97
Cadmium	Cd	48	112.4	Platinum	Pt	78	195.08
Calcium	Ca	20	40.08	Plutonium	Pu	94	r
Californium	Cf	98	r	Polonium	Po	84	r
Carbon	C	6	12.01	Potassium	K	19	39.10
Cerium	Ce	58	140.12	Praseodymium	Pr	59	140.91
Cesium	Cs	55	132.91	Promethium	Pm	61	r
Chlorine	Cl	17	35.45	Protactinium	Pa	91	231.04
Chromium	Cr	24	52.00	Radium	Ra	88	r
Cobalt	Co	27	58.93	Radon	Rn	86	r
Copper	Cu	29	63.55	Rhenium	Re	75	186.21
Curium	Cm	96	r	Rhodium	Rh	45	102.90
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.47
Einsteinium	Es	99	r	Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Samarium	Sm	62	150.36
Europium	Eu	63	151.96	Scandium	Sc	21	44.96
Fermium	Fm	100	r	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.09
Francium	Fr	87	r	Silver	Ag	47	107.87
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.99
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.61	Sulfur	S	16	32.07
Gold	Au	79	196.97	Tantalum	Ta	73	180.95
Hafnium	Hf	72	178.49	Technetium	Tc	43	r
Helium	He	2	4.00	Tellurium	Te	52	127.60
Holmium	Ho	67	164.93	Terbium	Tb	65	158.93
Hydrogen	H	1	1.01	Thallium	Tl	81	204.38
Indium	In	49	114.82	Thorium	Th	90	232.04
Iodine	I	53	126.90	Thulium	Tm	69	168.93
Iridium	Ir	77	192.22	Tin	Sn	50	118.71
Iron	Fe	26	55.85	Titanium	Ti	22	47.87
Krypton	Kr	36	38.80	Tungsten	W	74	183.84
Lanthanum	La	57	138.91	Uranium	U	92	238.03
Lead	Pb	82	207.2	Vanadium	V	23	50.94
Lithium	Li	3	6.94	Xenon	Xe	54	131.29
Lutetium	Lu	71	174.97	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.31	Yttrium	Y	39	88.91
Manganese	Mn	25	54.94	Zinc	Zn	30	65.39
Mendelevium	Md	101	258.10	Zirconium	Zr	40	91.22

r = radioactive, no stable isotopes. Source of data: *CRC Handbook of Chemistry and Physics*, 81st ed. (2000)

THE PERIODIC TABLE

GROUP: Common U.S. notation / International notation

G = Noble gas

N = Nonmetals

The rest are metals

Element Name
Atomic No. **Symbol**
Atomic weight
Density (solids & **liquids**, g/cm^3; Gases, g/l)
Melting Point (solids & **liquids**)/Boiling Point (gases) (°C)

PERIOD	IA 1	IIA 2		IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIIIB 8	VIIIB 9	VIIIB 10	IB 11	IIB 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	VIIIA 18
1	Hydrogen 1 **H** 1.0079 0.090 −252.87																		Helium 2 **He** 4.0026 *G* 0.177 −268.93
2	Lithium 3 **Li** 6.941 0.54 180.5	Beryllium 4 **Be** 9.0122 1.85 1287												Boron 5 **B** 10.811 *N* 2.46 2076	Carbon 6 **C** 12.011 *N* 2.27 3900	Nitrogen 7 **N** 14.007 *N* 1.251 −195.79	Oxygen 8 **O** 15.999 *N* 1.429 −182.95	Fluorine 17 **F** 18.998 *N* 1.696 −188.12	Neon 1 **Ne** 20.180 *G* 0.900 −246.08
3	Sodium 11 **Na** 22.990 0.97 97.7	Magnesium 12 **Mg** 24.305 1.74 650												Aluminum 13 **Al** 26.982 2.70 660.3	Silicon 14 **Si** 28.086 *N* 2.33 1414	Phosphorus 15 **P** 30.974 *N* 1.82 44.2	Sulfur 16 **H** 32.065 *N* 1.96 115.2	Chlorine 17 **Cl** 35.453 *N* 3.214 −34.04	Argon 18 **Ar** 39.948 *G* 1.784 −185.85
4	Potassium 19 **K** 39.098 0.86 63.4	Calcium 20 **Ca** 40.078 1.55 842		Scandium 21 **Sc** 44.956 2.99 1541	Titanium 22 **Ti** 47.867 4.51 1668	Vanadium 23 **V** 50.942 6.11 1910	Chromium 24 **Cr** 51.996 7.14 1907	Manganese 25 **Mn** 54.938 7.47 1246	Iron 26 **Fe** 55.845 7.87 1538	Cobalt 27 **Co** 58.933 8.90 1495	Nickel 28 **Ni** 58.693 8.91 1455	Copper 29 **Cu** 63.546 8.92 1084.6	Zinc 30 **Zn** 65.39 7.14 419.5	Gallium 31 **Ga** 69.723 5.9 29.8	Germanium 32 **Ge** 72.64 5.32 938.3	Arsenic 33 **As** 74.922 *N* 5.73 816.9	Selenium 34 **Se** 78.96 *N* 4.82 221	Bromine 35 **Br** 79.904 *N* 3.12 −7.3	Krypton 36 **Kr** 83.80 *G* 3.733 −153.22
5	Rubidium 37 **Rb** 85.468 1.53 39.3	Strontium 38 **Sr** 87.62 2.63 777		Yttrium 39 **Y** 88.906 4.47 1526	Zirconium 40 **Zr** 91.224 6.51 1855	Niobium 41 **Nb** 92.906 8.57 2477	Molybdenum 42 **Mo** 95.94 10.28 2623	Technetium 43 **Tc** [98] 11.6 2157	Ruthenium 44 **Ru** 101.07 12.37 2334	Rhodium 45 **Rh** 102.91 12.45 1964	Palladium 46 **Pd** 106.42 12.02 1554.9	Silver 47 **Ag** 107.87 10.49 961.8	Cadmium 48 **Cd** 112.41 8.65 321.1	Indium 49 **In** 114.82 7.31 156.6	Tin 50 **Sn** 118.71 7.31 231.9	Antimony 51 **Sb** 121.76 6.70 630.6	Tellurium 52 **Te** 127.60 *N* 6.24 449.5	Iodine 53 **I** 126.90 4.94 113.7	Xenon 54 **Xe** 131.29 *G* 5.887 −108.05
6	Cesium 55 **Cs** 132.91 1.88 28.4	Barium 56 **Ba** 137.33 3.51 727	57-70 *	Lutetium 71 **Lu** 174.97 9.84 1652	Hafnium 72 **Hf** 178.49 13.31 2233	Tantalum 73 **Ta** 180.95 16.65 3017	Tungsten 74 **W** 183.84 19.25 3422	Rhenium 75 **Re** 186.21 21.02 3186	Osmium 76 **Os** 190.23 22.61 3033	Iridium 77 **Ir** 192.22 22.65 2466	Platinum 78 **Pt** 195.08 21.09 1768.3	Gold 79 **Au** 196.97 19.30 1064.2	Mercury 80 **Hg** 200.59 **13.55** **−38.83**	Thallium 81 **Tl** 204.38 11.85 304	Lead 82 **Pb** 207.2 11.34 327.5	Bismuth 83 **Bi** 208.98 9.78 271.3	Polonium 84 **Po** [209] 9.20 254	Astatine 85 **At** [210] *N* – 302	Radon 86 **Rn** [222] *G* 9.73 −61.85
7	Francium 87 **Fr** [223] – –	Radium 88 **Ra** [226] 5.0 700	89-102 **	Lawrencium 103 **Lr** [262] – 1827	Rutherfordium 104 **Rf** [262] – –	Dubnium 105 **Db** [262] – –	Seaborgium 106 **Sg** [266] – –	Bohrium 107 **Bh** [264] – –	Hassium 108 **Hs** [277] – –	Meitnerium 109 **Mt** [268] – –	Darmstadtium 110 **Ds** [281] – –	Roentgenium 111 **Rg** [272] – –	Ununbium 112 **Uub** [285] – –	Ununtrium 113 **Uut** [284] – –	Ununquadium 114 **Uuq** [289] – –	Ununpentium 115 **Uup** [288] – –	Ununhexium 116 **Uuh** [292] – –	Ununseptium 117 **Uus** [?] – –	Ununoctium 118 **Uuo** [?] – –

*Lanthanoids	Lanthanum 57 **La** 138.91 6.146 920	Cerium 58 **Ce** 140.12 6.689 795	Praseodymium 59 **Pr** 140.91 6.64 935	Neodymium 60 **Nd** 144.24 6.80 1024	Promethium 61 **Bh** [145] 7.264 1100	Samarium 62 **Sm** 150.36 7.353 1072	Europium 63 **Eu** 151.96 5.244 826	Gadolinium 64 **Gd** 157.25 7.901 1312	Terbium 65 **Tb** 158.93 8.219 1356	Dysprosium 66 **Dy** 162.50 8.551 1407	Holmium 67 **Ho** 164.93 8.795 1461	Erbium 68 **Er** 167.26 9.066 1497	Thullum 69 **Tm** 168.93 9.321 1545	Ytterbium 70 **Yb** 173.04 6.57 824
**Actinoids	Actinium 89 **Ac** [227] 10.07 1050	Thorium 90 **Th** 232.04 11.72 1842	Protactinium 91 **Pa** 231.04 15.37 1568	Uranium 92 **U** 238.03 19.05 1132	Neptunium 93 **Np** [237] 20.45 637	Plutonium 94 **Pu** [244] 19.816 639	Americum 95 **Am** [243] – 1176	Curium 96 **Cm** [247] 13.51 1340	Berkelium 97 **Bk** [247] 14.78 986	Californium 98 **Cf** [251] 15.1 900	Einsteinium 99 **Es** [252] – 860	Fermium 100 **Fm** [257] – 1527	Mendelevium 101 **Md** [258] – 827	Nobelium 102 **No** [259] – 827

INTRODUCTION TO GEOCHEMISTRY

Introduction to Geochemistry

Principles and Applications

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1 2012

To

Anand, Lolly, and Tom

Brief Contents

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COMPANION WEBSITE

This book has a companion website

www.wiley.com/go/misra/geochemistry

with Figures and Tables from the book for downloading.

Preface

Geochemistry deals essentially with the processes and consequences of distribution of elements in minerals and rocks in different physical–chemical environments and, as such, permeates all branches of geology to varying degrees. An adequate background in geochemistry is, therefore, an imperative for earth science students. This book is an attempt to cater to that need. It covers a wide variety of topics, ranging from atomic structures that determine the chemical behavior of elements to modern biogeochemical cycles that control the global–scale distribution of elements. It is intended to serve as a text for an introductory undergraduate/graduate level course in geochemistry, and it should also provide the necessary background for more advanced courses in mineralogy, petrology, and geochemistry.

The organization of the book is logical and quite different from the geochemistry texts in the market. Excluding the "Introduction", the 12 chapters of the book are divided into four interrelated parts. Part I (Crystal Chemistry – Chapters 2 and 3) provides a brief review of the electronic structure of atoms and of different kinds of chemical bonds. Part II (Chemical Reactions – Chapters 4 through 9) discusses the thermodynamic basis of chemical reactions involving phases of constant and variable composition, including reactions relevant to aqueous systems and reactions useful for geothermometry and geobarometry. A substantial portion of the chapter on oxidation–reduction reactions (Chapter 8) is devoted to a discussion of the role of bacteria in such reactions. The last chapter of Part II is a brief introduction to the kinetic aspects of chemical reactions. Part III (Isotope Geochemistry – Chapters 10 and 11) introduces the students to radiogenic and stable isotopes, and their applications to geologic problems, ranging from dating of rocks and minerals to the interpretation of an anoxic atmosphere during the Hadean and Archean eras. Part IV (The Earth Supersystem – Chapters 12 and 13) is an overview of the origin and evolution of the solid Earth (core, mantle, and crust), and of the atmosphere and hydrosphere. A brief discussion of some important biogeochemical cycles provides a capstone to the introductory course.

The treatment in this book recognizes the welcome fact that geochemistry has become increasingly more quantitative, and assumes that the students have taken the usual selection of elementary courses in earth sciences, chemistry, and mathematics. Nevertheless, most relevant chemical concepts and mathematical relations are developed from first principles. It is my experience that the derivation of an equation enhances the appreciation for its applications and limitations. To maintain the flow of the text, however, some derivations and tangential material are separated from the text in the form of "boxes." Supplementary data and explanations are presented in 10 appendixes.

Quantitative aspects of geochemistry are emphasized throughout the book to the extent they are, in my judgment, appropriate at an introductory level.

Each chapter in the book contains many solved examples illustrating the application of geochemistry to real-life geological and environmental problems. At the end of each chapter is a list of computational techniques the students are expected to have learned and a set of questions to reinforce the importance of solving problems. It is an integral part of the learning process that the students solve every one of these problems. To help the students in this endeavor, answers to selected problems are included as an appendix (Appendix 10).

I owe a debt of gratitude to all my peers who took the time to review selected parts of the manuscript: D. Sherman, University of Bristol; D.G. Pearson, Durham University; Hilary Downes, University College (London); Harry McSween, Jr., University of Tennessee (Knoxville); and Harold Rowe, University of Texas (Arlington). Their constructive critiques resulted in significant improvement of the book, but I take full responsibility for all shortcomings of the book. Thanks are also due to many of my colleagues in the Department of Earth and Planetary Sciences, University of Tennessee – Christopher Fedo, Robert Hatcher, Linda Kah, Theodre Labotka, Colin Sumrall, and Lawrence Taylor – who in course of many discussions patiently shared with me their expertise on selected topics covered in the book. I am particularly grateful to Harry McSween for many

prolonged discussions regarding the origin and early history of the Earth, and to Ian Francis, Senior Commissioning Editor, Earth and Environmental Sciences, Wiley-Blackwell Publishers, for his sustained encouragement throughout this endeavor. I am also indebted to the many publishers and individuals who have kindly allowed me to include copyrighted figures in the book. Lastly, and most importantly, this book could not have been completed without the patience of my wife, children, and grandchildren, who had to endure my preoccupation with the book for long stretches.

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May 2011

1 Introduction

Geochemistry, as the name suggests, is the bridge between geology and chemistry and, thus, in essence encompasses the study of all chemical aspects of the Earth and their interpretation utilizing the principles of chemistry.

Rankama and Sahama (1950)

1.1 Units of measurement

A unit of measurement is a definite magnitude of a physical quantity, defined and adopted by convention and/or by law, that is used as a standard or measurement of the same physical quantity. Any other value of the physical quantity can be expressed as a simple multiple of the unit of measurement.

The original metric system of measurement was adopted in France in 1791. Over the years it developed into two somewhat different systems of metric units: (a) the *MKS system*, based on the meter, kilogram, and second for length, mass, and time, respectively; and (b) the *CGS system* (which was introduced formally by the British Association for the Advancement of Science in 1874), based on the centimeter, gram, and second. There are other traditional differences between the two systems, for example, in the measurements of electric and magnetic fields. The recurring need for conversion from units in one of the two systems to units of the other, however, defeated the metric ideal of a universal measuring system, and a choice had to be made between the two systems for international usage.

In 1954, the Tenth General Conference on Weights and Measures adopted the meter, kilogram, second, ampere, degree Kelvin, and candela as the basic units for all international weights and measures. Soon afterwards, in 1960, the Eleventh General Conference adopted the name *International System of Units* (abbreviated to *SI* from the French "Système International d'Unitès") for this collection of units. The "degree Kelvin" was renamed the "kelvin" in 1967.

1.1.1 *The SI system of units*

In the SI system, the modern form of the MKS system, there are seven base units from which all other units of measurement can be derived (Table 1.1). The International Union of Pure and Applied Chemistry (IUPAC) has recommended the use of SI units in all scientific communications. This is certainly desirable from the perspective of standardization of data, but a lot of the available chemical data were collected prior to 1960 and thus are not necessarily in SI units. It is therefore necessary for geochemists to be familiar with both SI and non-SI units. Equivalence between SI and non-SI units, and some of the commonly used physical constants are given in Appendix 1.

Most chemists, physicists, and engineers now use SI system of units, but the use of CGS (centimeter–gram–second) and other non-SI units is still widespread in geologic literature. In this book we will use SI units, but with two exceptions. As pointed out by Powell (1978) and Nordstrom and Munoz (1994), the SI unit pascal (Pa) is unwieldy for reporting geological pressures. For example, many geochemical measurements have been done at 1 atmosphere (atm) ambient pressure (the pressure exerted by the atmosphere at sea level), which translates into 101,325 pascals or 1.01 megapascals

Introduction to Geochemistry: Principles and Applications, First Edition. Kula C. Misra.

Table 1.1 The SI base units and examples of SI derived units.

SI base units			Examples of SI derived units			
Physical quantity	**Name**	**Symbol**	**Physical quantity**	**Name**	**Symbol**	**Definition in terms of the SI base units**
Length	Meter	m	Force	Newton	N	$m\ kg\ s^{-2}$
Mass	Kilogram	kg	Pressure	Pascal	Pa	$m^{-1}\ kg\ s^{-2} = Nm^{-2}$
Time	Second	s	Energy, work, heat	Joule	J	$m^2\ kg\ s^{-2} = Nm$
Temperature	Kelvin	K	Electric charge	Coulomb	C	sA
Amount of substance	Mole	mol	Electric potential difference	Volt	V	$m^2\ kg\ s^{-3}\ A^{-1}$
Electric current	Ampere	A	Volume	Liter	L	$m^3\ 10^{-3}$
Luminous intensity	Candela	cd	Electric conductance	Siemens	S	$m^{-2}\ kg^{-1}\ s^3\ A^2$

Newton = the force that will accelerate a mass of 1 kg by 1 m s^{-2}.
Pascal = the pressure exerted when a force of 1 N acts uniformly over an area of 1 m^2.
Joule = work done when a force of 1 N produces a displacement of 1 m in the direction of the force.

(Mpa), a rather cumbersome number to use. Most geochemists prefer to use bar as the unit of pressure, which can easily be converted into pascals (1 bar = 10^5 pascals or 0.1 MPa) and which is close enough to pressure expressed in atmosphere (1 bar = 0.987 atm) for the difference to be ignored in most cases without introducing significant error. A similar problem exists in the use of the SI unit joule (J), instead of the more familiar non-SI unit calorie (cal). The calorie, defined as the quantity of heat required to raise 1 gram (g) of water from 14.5 to 15.5°C, has a physical meaning that is easy to understand. Moreover, tables of thermodynamic data, especially the older ones, use calories instead of joules. Thus, we may use calories in the calculations and report the final results in joules (1 cal = 4.184 J).

The familiar scale of temperature is the Celsius scale (°C), which is based on two reference points for temperature: the *ice point*, the temperature at which ice is in equilibrium with liquid water at 1 atm pressure; and the *steam point*, the temperature at which steam is in equilibrium with liquid water at 1 atm pressure. The Celsius scale arbitrarily assigns a temperature of zero to the ice point and a temperature of 100 to the steam point. The SI unit of temperature is kelvin (K), which is the temperature used in all thermodynamic calculations. If pressure–temperature (°C) plots at different volumes are constructed for any gas, the extrapolated lines all intersect at a point representing zero pressure at a temperature around −273°C (Fig. 1.1). This temperature, which is not physically attainable (although it has been approached very closely), is called the *absolute zero of temperature*. It is the temperature at which the molecules of a gas have no translational, rotational, or vibrational motion and therefore no thermal energy. The temperature scale with absolute zero as the starting point is the *kelvin temperature scale* and the unit of temperature on this scale is kelvin (K, not °K), so named after Lord Kelvin who proposed it in 1848. The kelvin unit of temperature is defined as the 1/273.16 fraction of the so-called *triple point* for H_2O (the temperature at which ice, liquid water, and steam coexist in equilibrium at 1 atm pressure), which is 0.01 K greater than the ice point. Thus, the ice point, which is defined as 0°C, corresponds to 273.15 K (see Fig. 4.3) and the relationship between kelvin and Celsius scales of temperature is given by:

$$T\ (\mathrm{K}) = t\ (°\mathrm{C}) + 273.15 \tag{1.1}$$

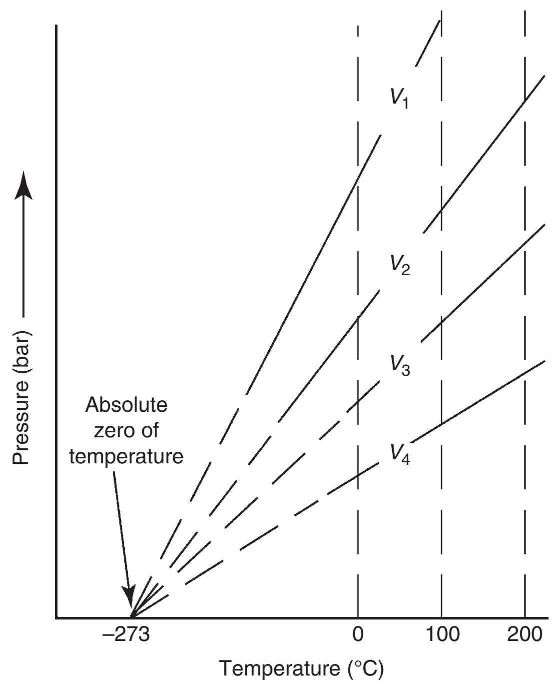

Fig. 1.1 The definition of absolute zero of temperature. The lines V_1–V_4 show the variation of different volumes of a gas as a function of temperature and pressure. When extrapolated, the lines intersect at a point representing zero pressure at a temperature around −273°C. This temperature, which is not physically attainable, is called the absolute zero of temperature.

Evidently, the steam point (100°C) corresponds to 373.15 K. It follows from equation (1.1) that the degree Celsius is equal in magnitude to the kelvin, which in turn implies that the numerical value of a given temperature difference or temperature interval is the same whether it is expressed in the unit degree Celsius (°C) or in the unit kelvin. (In the USA, temperatures are often measured in the Fahrenheit scale (F). The expression relating temperatures in the Celsius and Fahrenheit scales is: F=9/5°C+32.)

1.1.2 *Concentration units for solutions*

Concentrations of solutes (dissolved substances) in solutions (solids, liquids, or gases) are commonly expressed either as mass concentrations (parts per million, or milligrams per liter, or equivalent weights per liter) or as molar concentrations (*molality*, *molarity*, or *mole fraction*; Table 1.2).

To obtain the number of moles (abbreviated *mol*) of a substance, the amount of the substance (in grams) is divided by its gram-molecular weight; to obtain the mole fraction of a substance, the number of moles of the substance is divided by the total number of moles in the solution (see section 2.2 for further elaboration). For example, the mole fraction of NaCl (gram-molecular weight=58.44) in a solution of 100 g of NaCl in 2 kg of H_2O (gram-molecular weight=18.0) can be calculated as follows:

Number of moles of NaCl=100/58.44=1.7112
Number of moles of H_2O=2 (1000)/18.0=111.1111
Total number of moles in the solution= 1.7112 + 111.1111 = 112.8223
Mole fraction of NaCl in solution=1.7112 /112.8223=0.0152

Note that the mole fraction of a pure substance (solid, liquid, or gas) is unity.

The concentration units mg/L and ppm, as well as molality and molarity, are related through the density of the solution (ρ):

$$\text{concentration (ppm)} = \frac{\text{concentration of solute (g L}^{-1})}{\rho \text{ (g mL}^{-1})} \quad (1.2)$$

$$m = M\left(\frac{\text{weight of solution (g)}}{\text{weight of solution (g)} - \text{total weight of solutes (g)}}\right)\left(\frac{1}{\rho \text{ (g mL}^{-1})}\right) \quad (1.3)$$

Concentrations expressed in molality or mole fraction have the advantage that their values are independent of temperature and pressure; molarity, on the other hand, is dependent on the volume of the solution, which varies with temperature and pressure. The advantage of using molarity is that it is often easier to measure the volume of a liquid than its weight. For dilute aqueous solutions at 25°C, however, the density of the solution is very close to that of pure water, ρ=(1 kg)/(l L), so that little error is introduced if the difference between mg/L and ppm or molality and molarity is ignored for such a solution.

The strength of an acid or a base is commonly expressed in terms of *normality*, the number of equivalent weights of the acid or base per liter of the solution, the *equivalent weight* being defined as the gram-molecular weight per number of Hs or OHs in the formula unit. For example, the equivalent weight of H_2SO_4 (gram-molecular weight=98) is 98/2=49, and the normality of a solution of 45 g of H_2SO_4 in 2 L of solution is 45/(49×2)=0.46.

Table 1.2 Concentration units for a solute.

Concentration unit	Definition
Milligrams per liter (mg/L)	Mass of solute (mg) / volume of solution (L)
Parts per million (ppm)	Mass of solute (mg) / mass of solution (kg)
Mole fraction (*X*)	Moles of solute / total moles of solution[1]
Molarity (*M*)	Moles of solute / volume of solution (L)
Molality (*m*)	Moles of solute / mass of solvent (kg)
Normality (*N*)	Equivalent weight of solute (g) / volume of solution (L)

[1]Moles of a substance=weight of the substance (g)/gram-molecular weight of the substance.

1.2 The Geologic Time Scale

Discussions of events require a timeframe for reference. The Geologic Time Scale provides such a reference for past geologic events. Forerunners of the current version of the time scale were developed in small increments during the 19th century, long before the advent of radiometric dating, using techniques applicable to determining the relative order of events. These techniques are based on the principles of *original horizontality* (sediments are deposited in horizontal layers), *superposition* (in a normal sequence of sedimentary rocks or lava flows, the layer above is younger than the layer below), and *faunal succession* (fossil assemblages occur in rocks in a definite and determinable order). Although the time scale evolved haphazardly, with units being added or modified in different parts of the world at different times, it has been organized into a universally accepted workable scheme of classification of geologic time.

The Geologic Time Scale spans the entire interval from the birth of the Earth (t=4.55 Ga, i.e., 4.55 billion years before the present) to the present (t=0), and is broken up into a hierarchical set of relative time units based on the occurrence of distinguishing geologic events. Generally accepted divisions for increasingly smaller units of time are *eon*, *era*, *period*, and *epoch* (Fig. 1.2). Different spans of time on the time scale are usually delimited by major tectonic or paleontological events

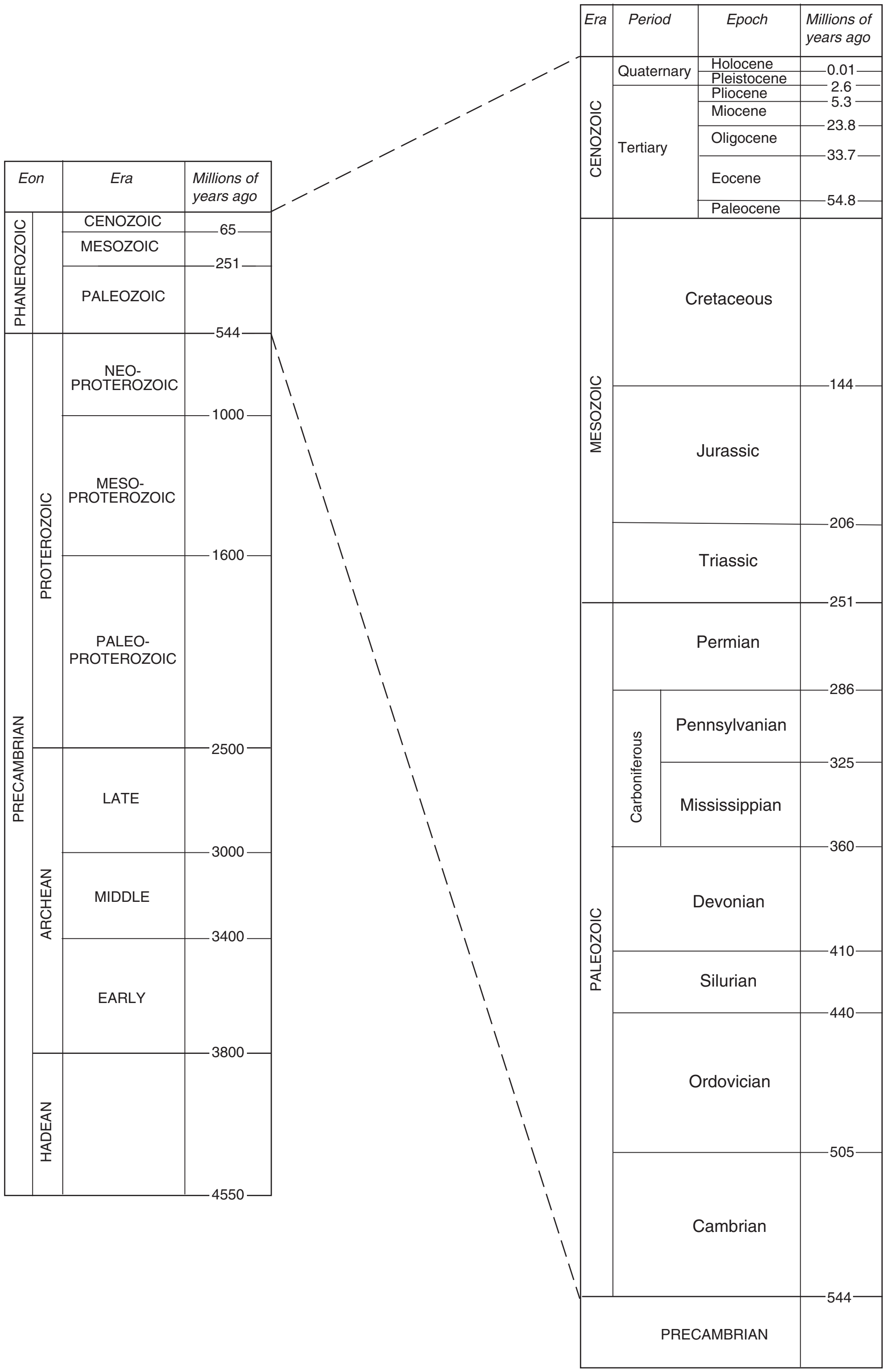

Fig. 1.2 The Geologic Time Scale. The age of the Earth, based on the age of meteorites, is 4.55 ± 0.05 Ga according to Patterson (1956) and 4.55–4.57 Ga according to Allègre *et al.* (1995).

such as orogenesis (mountain–building activity) or mass extinctions. For example, the Cretaceous–Tertiary boundary is defined by a major mass extinction event that marked the disappearance of dinosaurs and many marine species.

Absolute dates for the boundaries between the divisions were added later on, after the development of techniques for dating rocks using radioactive isotopes (see Chapter 10). The time scale shown in Fig. 1.2 includes these dates, producing an integrated geologic time scale. Time units that are older than the Cambrian Period (that is, units in the Precambrian Eon) pre-date reliable fossil records and are defined by absolute dates.

1.3 Recapitulation

Terms and concepts

Absolute zero of temperature
Celsius scale (temperature)
CGS system of units
Eon
Epoch
Era
Equivalent weight
Fahrenheit scale (temperature)
Faunal succession
Geologic Time Scale
Fahrenheit scale (temperature)
Geologic time scale
Gram–molecular weight
Kelvin scale (temperature)
Mass concentration
Mass extinction
MKS system of units
Molality
Molarity
Mole
Mole fraction
Original horizontality
Period
SI units
Superposition

Computation techniques

- Conversion of SI units to non-SI units.
- Conversion of °C to °F and K.
- Calculations of number of moles, mole fraction, molarity, molality, ppm.

1.4 Questions

Gram atomic weights: H = 1.0; C = 12.01; O = 16.00; Na = 22.99; Al = 26.98; Si = 28.09; S = 32.07; Cl = 35.45; K = 39.10; Ca = 40.08.

1. The gas constant, R, has the value 1.987 cal K^{-1} mol^{-1}. Show that

   $$R = 8.317 \text{ Joules } K^{-1} \text{ mol}^{-1} = 8.317 \times 10^7 \text{ ergs } K^{-1} \text{ mol}^{-1} = 83.176 \text{ cm}^3 \text{ bar } K^{-1} \text{ mol}^{-1}$$

2. Show that (a) 1 calorie $bar^{-1} = 41.84\,cm^3$, and (b) $1\,m^3 =$ 1 joule $pascal^{-1}$
3. What is the molarity of one molal NaCl solution (at 25°C and 1 bar)? Density of the NaCl solution (at 25°C and 1 bar) is 1.0405 kg L^{-1}.
4. What are the mole fractions of C_2H_5OH (ethanol) and H_2O (water) in a solution prepared by mixing 70.0 g of ethanol with 30.0 g of water?
5. What are the mole fractions of C_2H_5OH (ethanol) and H_2O (water) in a solution prepared by mixing 70.0 mL of ethanol with 30.0 mL of water at 25°C? The density of ethanol is 0.789 g mL^{-1}, and that of water is 1.00 g mL^{-1}.
6. When dissolved in water, NaCl dissociates into Na^+ and Cl^- ions ($NaCl = Na^+ + Cl^-$). What is the molality of Na^+ in a solution of 1.35 g of NaCl dissolved in 2.4 kg of water? What is the concentration of Na^+ the solution in ppm?
7. The density of an aqueous solution containing 12.5 g K_2SO_4 in 100.00 g solution is 1.083 g mL^{-1}. Calculate the concentration of K_2SO_4 in the solution in terms of molality and molarity. What is the mole fraction of the solvent in the solution?
8. The ideal chemical formula of the mineral albite is $NaAlSi_3O_8$. How many moles of $NaAlSi_3O_8$ do 5 g of the mineral contain? How many moles of Si?
9. A solution made by dissolving 16.0 g of $CaCl_2$ in 64.0 g of water has a density of 1.180 g mL^{-1} at 25°C. Express the concentration of Ca in the solution in terms of molality and molarity.

Part I
Crystal Chemistry

The task of crystal chemistry is to find systematic relationships between the chemical composition and physical properties of crystalline substances, and in particular to find how crystal structure, i.e., the arrangement of atoms or ions in crystals, depend on chemical composition.

Goldschmidt (1954)

2 Atomic Structure

I knew of [Heisenberg's) theory, of course, but I felt discouraged, not to say repelled, by the methods of transcendental algebra, which appeared difficult to me, and by the lack of visualizability (Edwin Schrödinger, 1926).

The more I think about the physical portion of Schrödinger's theory, the more repulsive I find it.... What Schrödinger writes about the visualizability of his theory is probably not quite right, in other words it's crap (Werner Heisenberg, 1926).

[Extracted from the worldwide web]

The three major physical states in which a system (part of the universe that we have chosen for consideration) occurs are solid, liquid, and gaseous. Although we commonly think of distinctions among the three states in terms of physical properties such as bounding surface, hardness, viscosity, etc., the fundamental difference lies in the arrangement of atoms in the three states. *Crystalline* solids, which can occur spontaneously in a form bounded by planar surfaces, are characterized by *long-range order*, a regularity in the arrangement of atoms or molecules that is repeated along parallel lines. *Amorphous* solids consist of extremely small solid units with a very small number of atoms per unit, so that "the forces which lead to the planar surfaces of solids and their internal order are destroyed by the enormous number of atoms in surface position" (Fyfe, 1964). Gases have no unique volume or boundaries, except those imposed by the chosen container; they lack ordering of their atoms or molecules. The liquid state may be viewed as being somewhere in between the solid and gaseous states. The atoms and molecules of liquids show only *short-range order*, i.e., ordering of the atoms and molecules extend only over a few molecular diameters. From the atomic perspective, *glass* may be regarded as a very viscous fluid. Our focus here is on crystalline solids because minerals, the main constituents of rocks, are by definition crystalline solids. We begin with a discussion of the general features of atomic structures because the physical and chemical properties of minerals are determined by the structure and arrangement of their constituent atoms.

2.1 Historical development

2.1.1 Discovery of the electron

The Greek philosopher Democritus (5th century BC) believed in the existence of four elementary substances – air, water, stone, and fire – all formed by a very large number of very small particles called *atoms*, the word for "indivisibles" in Greek (Gamow, 1961). Our understanding of the atom was not much better until about the beginning of the 20th century. Sir Isaac Newton (1642–1727) described atoms as "solid, massy, hard, impenetrable, moveable particles" and this was the generally accepted view throughout the 19th century.

In 1897, the British scientist J. J. Thompson (1856–1940), one of the pioneers in the investigation of atomic structure, proved by direct experiments that atoms are complex systems composed of positively and negatively charged parts. The experimental set-up, a primitive version of the modern television tube, was rather simple. It consisted of a glass tube containing highly rarified gas with a cathode (–) placed at one end, an anode (+) in the middle part, and a fluorescent screen at the other end (Fig. 2.1). When an electric current was passed through the gas in the tube, the fluorescent screen became luminous because of bombardment by fast moving particles resulting from the gas. When a piece of metal was placed in the path of the moving particles, it cast a shadow on the fluorescent screen, indicating a straight-line path for the particles

Introduction to Geochemistry: Principles and Applications, First Edition. Kula C. Misra.

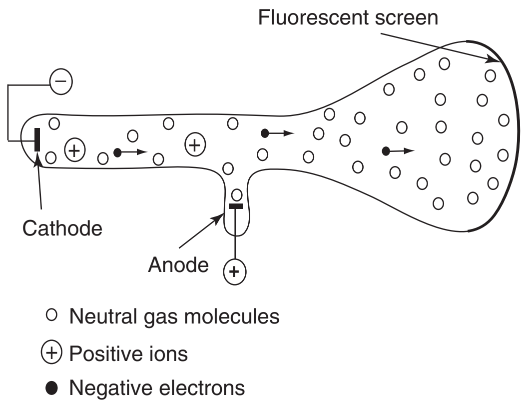

Fig. 2.1 Thompson's experimental set-up to study the effect of electric current on rarefied gas.

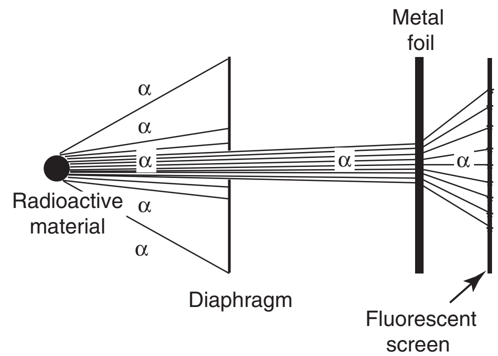

Fig. 2.2 Rutherford's experimental set-up for studying the scattering of α-particles emitted from a radioactive source.

in question, similar to light rays. Thompson visualized the atom as a complex system consisting of a positively charged substance (positive electric fluid) distributed uniformly over the entire body of the atom, with negatively charged particles (*electrons*) embedded in this continuously positive charge like seeds in a watermelon (Gamow, 1961). The model, however, was soon found to be unsatisfactory as the theoretically calculated optical line spectra (a set of characteristic light frequencies emitted by an "excited" atom) of different elements based on this model could not be matched with the observed optical spectra. Thompson also conducted experiments to determine the charge : mass ratio (*e/m*) of an electron (1.76×10^{-8} coulomb g^{-1}). A few years later, Robert A. Millikan experimentally measured the charge of an electron (1.602×10^{-19} coulomb) and computed its mass (about $9.109\times10^{-28}\,g^{-1}$).

2.1.2 *The Rutherford–Bohr atom*

In 1911, Ernest Rutherford (1871–1937), a New Zealand–born physicist, advanced the concept that the mass of an atom is concentrated at its center, which he named the *nucleus*. The experimental set-up that led to this discovery was quite simple (Fig. 2.2). A small amount of radioactive material emitting α-particles (positively charged helium ions that are ejected from the nucleus of an atom if it undergoes radioactive decay) was put on a pinhead and placed at a certain distance from a thin foil made from the metal to be investigated. The beam of α-particles was collimated by passing it through a lead diaphragm. A fluorescent screen was placed behind the foil to record the α-particles that would pass through the foil, each α-particle producing a little spark (scintillation) on the screen at the point of impact that could be viewed with the help of a microscope. In his experiments, Rutherford noticed that the majority of the α-particles passed through the foil almost without deflection, but some were deflected considerably and in a few cases (with a somewhat different experimental arrangement) some α-particles bounced back toward the source. Rutherford reasoned that collisions between the α-particles of the beam and the atoms of the target could not possibly deflect the incident particles by more than a few degrees; the observed large deflections required strong electrostatic repulsion between the positive charge of the bombarded atom and the positive charge of the incident α-particles. He concluded that the positive charge of the atom (associated with most of its mass) was not distributed throughout its body, as Thompson had envisaged, but had to be concentrated in a small central region of the atom, which he called the "atomic nucleus." It followed that the rest of the atom must be composed of a bunch of negatively charged electrons, rotating around the nucleus at high velocities so as not to fall into the positively charged nucleus because of electrostatic attraction. The positive charge of the nucleus was attributed to subatomic particles called *protons*. Rutherford speculated that the nucleus might also contain electrically neutral particles, although such elementary particles, called *neutrons*, were discovered only in 1932. Thus, the atomic model proposed by Rutherford consisted of negatively charged, light electrons whirling at very high velocities in circular paths around a positively charged, heavy nucleus at the center, so that the outward centrifugal force associated with such a motion would balance the electrostatic attraction between the electrons and the nucleus.

Rutherford's model, however, faced a serious problem because of the inherent instability of an electron orbiting around a positively charged nucleus. According to the laws of classical physics, such an electron would lose energy by emitting an electromagnetic wave, resulting in an increase in the velocity of the electron and a decrease in the radius of its orbit until the electron falls into the nucleus. Consider the hydrogen atom consisting of a bare proton and a single electron of mass m_e and charge e orbiting the nucleus of circular path of radius r at velocity v_e (Fig. 2.3). For this system, the energy of the atom (E_{atom}) is inversely proportional to the radius of the orbit (see Box 2.1):

$$E_{atom} = -\frac{1}{2}\left(\frac{e^2}{r}\right) = -\frac{1}{2}m_e v_e^2 \qquad (2.1)$$

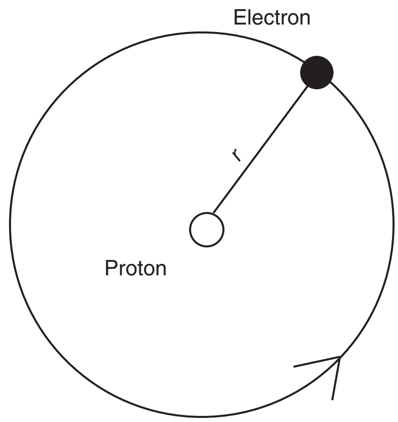

Fig. 2.3 Model of a hydrogen atom with a single electron moving in a circular orbit of radius r around a nucleus consisting of one proton.

Box 2.1 Derivation of equation for E_{atom}

Let us consider an electron of mass m_e and charge e orbiting around the nucleus of an atom in a circular path of radius r at velocity v_e (Fig. 2.3). The condition of stability for such an atom is that the force of attraction between the proton and electron (e^2/r^2) must be balanced by the centrifugal force($m_e v_e^2/r^2$):

$$\frac{e^2}{r^2} = \frac{m_e v_e^2}{r} \tag{2.2}$$

The energy of the system is the sum of the kinetic energy (1/2 $m_e v_e^2$) and potential energy ($-e^2/r$):

$$E_{atom} = \frac{1}{2} m_e v_e^2 - \frac{e^2}{r} \tag{2.3}$$

The potential energy term has a negative sign because the force between the proton in the nucleus and the electron is due to electrostatic attraction, which by convention is assigned a negative sign. Substituting the value of m_e from equation (2.2), $m_e = e^2/rv_e^2$ we get

$$E_{atom} = \frac{1}{2}\left(\frac{e^2}{r}\right) - \frac{e^2}{r} = -\frac{1}{2}\left(\frac{e^2}{r}\right) = -\frac{1}{2} m_e v_e^2 \tag{2.1}$$

Thus, the energy of the atom is negative and is inversely related to the radius of the orbit. The atom should become more stable as r decreases, and the electron should gradually fall into the nucleus. Calculations using classical physics predicted that electrons orbiting around a positively charged nucleus would lose all their energy in the form of electromagnetic waves within about one-hundred-millionth of a second and collapse into the nucleus.

The Danish physicist Neils Bohr (1885–1962), who had joined Rutherford as a postdoctoral fellow after a falling out with Thompson at the Cavendish Laboratory, Cambridge, provided the answer by applying Max Planck's revolutionary theory of quantization of electromagnetic energy. Speaking at the meeting of the German Physical Society on December 14, 1900, Max Planck (1858–1947) had proposed that light energy can exist only in the form of discrete packages, which he called "light quanta," and that the amount of energy of a light quantum (E) is directly proportional to the frequency (ϑ) of the radiation and inversely proportional to its wave length (λ). Since wavelength and frequency for light waves are related by the equation $\lambda\vartheta = c$, we have (see section 13.1.2)

$$E = h\vartheta = \frac{hc}{\lambda} \tag{2.4}$$

where h is the proportionality constant known as the Planck's Constant ($h = 6.62517 \times 10^{-34}$ J s), c is the speed of light "($c = 3 \times 10^{10}$ cm s^{-1}), λ is expressed in angstrom units (1 Å $= 10^{-8}$ cm), and E is in units of kiloelectron volts (keV). (Electron and X-ray energies are expressed in electron volts, 1 eV being the kinetic energy gained by a single unbound electron when it accelerates through an electric potential difference of 1 volt.) In his first article on the *Theory of Relativity* in 1905, Albert Einstein (1879–1955) had also used the quantum theory to explain empirical laws of the photoelectric effect, the emission of electrons from metallic surfaces irradiated by violet or ultraviolet rays. Bohr reasoned that, if the electromagnetic energy is *quantized* – i.e., permitted to have only certain discrete values – mechanical energy must be quantized too, although perhaps in a somewhat different way. After struggling with the idea for almost two years, he finally published it in 1913 (Bohr, 1913a,b). Bohr retained Rutherford's concept of electron motion in circular orbits (but rejected the classical law that moving charged particles radiate energy), and postulated that electrons moving around the atomic nucleus can reside only in a few permitted circular orbits or "shells," each with a specific level of energy (E_n) and a radius (r_n) given by (for a hydrogen atom, which has only one electron):

$$E_n = -\frac{2\pi^2 m_e e^4}{h^2 n^2} \tag{2.5}$$

$$r_n = \frac{h^2 n^2}{4\pi^2 m_e e^4} \tag{2.6}$$

where m_e is the mass of the electron, e is the magnitude of its charge, h is Planck's Constant, and n is the *principal quantum number* (see section 2.2.1) that can assume only integral values (1, 2, 3, …), each value of n defining a particular energy level for the electron. Note that the closer an orbit is to the nucleus (i.e., as the value of n gets smaller), the larger is E_n in absolute value but actually smaller in arithmetic value because of the negative sign (an arbitrary convention for attractive forces). The smallest radius permitted by Bohr's theory, the so-called *Bohr radius* (r_0), is obtained from equation (2.6) by setting $n = 1$. This is the radius of the orbit ($r_0 = 0.529 \times 10^{-8}$ cm) with the lowest permitted energy and thus represents the most stable state. The orbits corresponding to $n=1, 2, 3, \ldots, 7$ are sometimes referred to as $K, L, M, \ldots, Q$ "shells", respectively. An essential feature of the model is that an orbit of principal quantum number n can accept no more that $2n^2$ electrons. Bohr postulated further that an electron moving around the nucleus in a particular orbit is prohibited from emitting any electromagnetic radiation, but it does emit a quantum of monochromatic radiation when it jumps from an orbit of higher energy, say E_1, to an orbit of lower energy, say E_2, according to the relation derived earlier by Einstein:

$$E_1 - E_2 = \Delta E = h\vartheta \tag{2.7}$$

where ϑ is the frequency of the radiation and h is the Planck's Constant. Bohr's model of the atom provided a convincing explanation for the emission of X-rays (which had been discovered by William Konrad Röntgen in1895) from target elements bombarded with a stream of electrons, and for the characteristic X-ray spectra of elements (Charles G. Barkla, 1911), which constitute the theoretical basis of modern electron microprobe and X-ray fluorescence analytical techniques.

Bohr's notion of circular quantum orbits worked very well for the hydrogen atom, the simplest of all atoms containing a single electron. By this time, the optical line spectra for hydrogen was well known from spectroscopic studies, and the spectra predicted from Bohr's model was a perfect match. The model, however, broke down almost completely for atoms having two or more electrons. Soon after, to allow more freedom in choosing the "permitted" orbits for multi-electron atoms, Arnold Sommerfeld (1868–1951) introduced the idea of elliptical orbits, which had different geometrical shapes but corresponded to almost the same energy levels as Bohr's circular orbits. According to Sommerfeld's postulate, the orbit closest to the nucleus ($n=1$) is circular and corresponds to the lowest energy of the electron. The next four orbits ($n=2$), one circular and the other three energetically equivalent but elliptical, have higher energy than that associated with the first orbit; the next nine orbits ($n=3$), one circular and the rest eight energetically equivalent but elliptical, correspond to a still higher level of energy, and so on (see Table 2.2 and Fig. 2.7).

2.1.3 Wave mechanics

In a doctoral thesis presented in 1925, Louis Victor de Broglie (1892–1987) proposed a new interpretation of Bohr's quantum orbits. He postulated that each electron moving along a given orbit is accompanied by some mysterious "pilot waves" (now known as *de Broglie waves*), whose propagation velocity and wavelength depend on the velocity of the electron in question. He deduced that the wavelength λ of an electron of mass m_e and velocity v_e is inversely proportional to its momentum ($m_e v_e$) and related to Planck's Constant (h) by the equation:

$$\lambda = \frac{h}{m_e v_e} \tag{2.8}$$

The validity of this relationship was confirmed later by experiments demonstrating diffraction effects for electrons similar to those of X-rays. A year later, in 1926, de Broglie's ideas were brought into more exact mathematical form by Werner Heisenberg (1901–1976) and Edwin Schrödinger (1887–1961). The two scientists used entirely different formulations but arrived at the same results concerning atomic structure and optical spectra. Heisenberg developed the *Uncertainty Principle*, which states that the position and velocity of an electron in motion, whether in a circular or in an elliptical orbit, cannot be measured simultaneously with high precision. The mathematical formulation, however, was abstract and relied on matrix algebra. Most physicists of the time were slow to accept "matrix mechanics" because of its abstract nature and its unfamiliar mathematics. They gladly embraced Schrödinger's alternative wave mechanics, since it entailed more familiar concepts and equations, and it seemed to do away with quantum jumps and discontinuities. However, Schrödinger soon published a proof that matrix mechanics and wave mechanics gave equivalent results: mathematically they were the same theory, although he argued for the superiority of wave mechanics over matrix mechanics.

The recognition of the wave-like nature of the electron forced a fundamental change in ideas regarding the distribution of electrons in an atom. The concept of electrons as physical particles moving in orbits of definite geometrical form was replaced by a probability distribution of electron density (the number of electrons per unit volume) around the nucleus, rendering it possible to calculate the probability of finding the position of the electron at any point around the nucleus. From classical equations governing the behavior of waves, Schrödinger developed a general equation for de Broglie waves and proved its validity for all kinds of electron motion in three-dimensional space. Schrödinger's theory, which has now become known as *wave mechanics* (or *quantum mechanics*), explains not only all the atomic phenomena for which Bohr's model works, but also those phenomena (such as intensities of optical spectral lines) for which Bohr's model does not. In its most commonly used form (Fyfe, 1964),

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m_e}{h^2}(E-V)\psi = 0 \tag{2.9}$$

the Schrödinger's wave equation, in essence, is a differential equation that relates a quantity ψ, the "wave function" of the system, to its total energy E and potential energy V. As defined earlier, m_e is the mass of the electron, h is Planck's Constant, and n is the principal quantum number. Such an equation can be satisfied by an infinite number of values of ψ, which lead to separate (not continuous) values of E for a given potential V. Of greatest interest are those solutions that yield the lowest possible values of E, the stable stationary state. The significance of ψ for our purpose lies in the fact that the value of ψ^2 at any point in space is a measure of the probability of finding