This book is intended to serve as a text for an introductory course in geochemistry for undergraduate/graduate students with at least an elementary-level background in earth sciences, chemistry, and mathematics. The text, containing 83 tables and 181 figures, covers a wide variety of topics—ranging from atomic structure to chemical and isotopic equilibria to modern biogeochemical cycles—which are divided into four interrelated parts: Crystal Chemistry; Chemical Reactions (and biochemical reactions involving bacteria); Isotope Geochemistry (radiogenic and stable isotopes); and The Earth Supersystem, which includes discussions pertinent to the evolution of the solid Earth, the atmosphere, and the hydrosphere.

In keeping with the modern trend in the field of geochemistry, the book emphasizes computational techniques by developing appropriate mathematical relations, solving a variety of problems to illustrate application of the mathematical relations, and leaving a set of questions at the end of each chapter to be solved by students. However, so as not to interrupt the flow of the text, involved chemical concepts and mathematical derivations are separated in the form of boxes. Supplementary materials are packaged into ten appendixes that include a standard-state (298.15 K, 1 bar) thermodynamic data table and a listing of answers to selected chapter-end questions.

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Actinoids: Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No
INTRODUCTION TO GEOCHEMISTRY
Introduction to Geochemistry
Principles and Applications

Kula C. Misra
Emeritus Professor, Department of Earth and Planetary Sciences,
The University of Tennessee, Knoxville, Tennessee, USA
To

Anand, Lolly, and Tom
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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.
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).

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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’Unités”) 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

(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:

\[ T(K) = t(°C) + 273.15 \]  

(1.1)
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: \( F = 9/5°C + 32 \).)

### 1.2 The Geologic Time Scale

#### 1.2.1 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 \( \text{mol} \)) 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 H₂O (gram-molecular weight = 18.0) can be calculated as follows:

- Number of moles of NaCl = \( 100 / 58.44 = 1.7112 \)
- Number of moles of H₂O = \( 2 \times (1000) / 18.0 = 111.1111 \)
- 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 (\( \rho \)):

\[
\text{concentration (ppm)} = \frac{\text{concentration of solute (g L\(^{-1}\))}}{\rho \text{ (g mL\(^{-1}\)}} \tag{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) \tag{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, \( \rho = (1\text{kg})/(1\text{L}) \), 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 H₂SO₄ (gram-molecular weight = 98) is 98/2 = 49, and the normality of a solution of 45 g of H₂SO₄ in 2 L of solution is 45/(49×2) = 0.46.

#### 1.2.2 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 (\( t = 4.55 \text{Ga} \), 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...
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 cm³, and (b) 1 m³=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 C₂H₅OH (ethanol) and H₂O (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 C₂H₅OH (ethanol) and H₂O (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 K₂SO₄ in 100.00 g solution is 1.083 g mL⁻¹. Calculate the concentration of K₂SO₄ 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 NaAlSi₃O₈. How many moles of NaAlSi₃O₈ do 5 g of the mineral contain? How many moles of Si?

9. A solution made by dissolving 16.0 g of CaCl₂ 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.
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

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.
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\( \times 10^{-8} \) coulomb g\(^{-1} \)). A few years later, Robert A. Millikan experimentally measured the charge of an electron (1.602\( \times 10^{-19} \) coulomb) and computed its mass (about 9.109\( \times 10^{-28} \) 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 \( \alpha \)-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 \( \alpha \)-particles was collimated by passing it through a lead diaphragm. A fluorescent screen was placed behind the foil to record the \( \alpha \)-particles that would pass through the foil, each \( \alpha \)-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 \( \alpha \)-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 \( \alpha \)-particles bounced back toward the source. Rutherford reasoned that collisions between the \( \alpha \)-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 \( \alpha \)-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 \( E_{\text{atom}} \) is inversely proportional to the radius of the orbit (see Box 2.1):

\[
E_{\text{atom}} = -\frac{1}{2}\left(\frac{e^2}{r}\right) = -\frac{1}{2}m_ev_e^2
\]  

or
2.1 Historical development

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 ($\nu$) of the radiation and inversely proportional to its wave length ($\lambda$). Since wavelength and frequency for light waves are related by the equation $\lambda \nu = c$, we have (see section 13.1.2)

$$E = h\nu = \frac{hc}{\lambda}$$

(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$^{-1}$), $\lambda$ 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):

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

(2.5)

$$r_n = \frac{b^2 n^2}{4\pi^2 m_e e^3}$$

(2.6)

where $m_e$ is the mass of the electron, $e$ is the magnitude of its charge, $b$ 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., 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 ($r_1$), is obtained from equation (2.6) by setting $n = 1$. This is the radius of the orbit ($r_1 = 0.529 \times 10^{-8}$ cm) with the lowest permitted energy and thus represents the most

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**Box 2.1 Derivation of equation for $E_{\text{atom}}$**

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 ($m_e v_e^2 r^2$):

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

(2.2)

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

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

(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), $m_e = e^2/4\pi^2 e^3$, we get

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

(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 Niels 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

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**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.
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 than \( 2n^2 \) 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:

\[
E_1 - E_2 = h \nu
\]

(2.7)

where \( \nu \) 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 in 1895) 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 \( \lambda \) of an electron of mass \( m_e \) and velocity \( \nu_e \) is inversely proportional to its momentum \( m_e \nu_e \) and related to Planck’s Constant \( (h) \) by the equation:

\[
\lambda = \frac{h}{m_e \nu_e}
\]

(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),

\[
\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{b^2} (E-V) \psi = 0
\]

(2.9)

the Schrödinger’s wave equation, in essence, is a differential equation that relates a quantity \( \psi \), 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, \( n \) is the principal quantum number. Such an equation can be satisfied by an infinite number of values of \( \psi \), 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 \( \psi \) for our purpose lies in the fact that the value of \( \psi^2 \) at any point in space is a measure of the probability of finding