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Chemical
Principles and Properties

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Chemical Principles and Properties

Second Edition

Chemical Principles and Properties

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3 4 5 6 7 8 9 0 DODO 7 9 8 7 6

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and all other drawings were done by Vantage Art, Inc.
R. R. Donnelley & Sons Company was printer and binder.

Library of Congress Cataloging in Publication Data

Sienko, Michell J
Chemical principles and properties.

First ed. published in 1966 under title:
Chemistry: principles and properties.
Bibliography: p.
1. Chemistry. I. Plane, Robert A., joint author. II. Title.
QD31.2.S558 1974 540 73-18479
ISBN 0-07-057364-6

The illustration on the cover is a photomicrograph of a silicon-carbide crystal developed by vapor-phase condensation. The spiral pattern of contour lines show the spiral pattern of crystal growth. The "rainbow" lines indicate crystal growth along lines of stress. The vari-colored patches at left bottom and right mark impurities in the crystal. Silicon carbide is used extensively in heavy-duty industrial abrasives. The magnification is approximately 1400 diameters. The micrograph was made by the late F. Hubbard Horn and is shown here through the courtesy of the General Electric Research and Development Center, Schenectady, New York.

Preface

The foundations of this book appeared almost 20 years ago as a set of notes for a new freshman chemistry course at Cornell University. It was the time of Sputnik, and there was excitement in the air as the traditional descriptive approach of beginning chemistry gave way to new points of view based on principles. A rather complete shift has occurred. Some have said it has gone too far, for, as ever is the case, high school courses have followed the college model, and descriptive chemistry has all but vanished from the curriculum.

We now stand in the wake of another upheaval, this time social and political but characterized also by disillusionment with science. Part of the disenchantment stemmed from the fact that science was oversold—it did not produce quick and easy answers as expected to the hard questions of society in turmoil. Also, however unjustified it may have been, it was easy to point to science as the initiator of material demands that led to pollution and degradation of the quality of the environment. A large segment of society turned its back on science, labeling it intrinsically bad because it was nonhumanitarian, dispassionate, and not involved. In the most simplistic view, it was said to be not relevant. Still, the problems did not go away. Populations increase; the tasks of feeding, housing, and giving health care become more pressing, more complicated, and more frustrating. The banning of DDT in one country leads to an increase in the incidence of malaria in another. How will these problems be solved, and by whom? Rather than rejecting science, which over the past 3 centuries has consistently demonstrated ability to solve problems, society is better served by turning to science to see how its methods can be applied to maximize the common good.

The first edition of "Chemical Principles and Properties" (called "Chemistry: Principles and Properties") was written to take advantage of increased sophistication in the prior chemical training of entering college students. This second edition recognizes that this sophistication is neither so deep nor so wide as previously supposed. Therefore, some of the subjects (e.g., atomic structure, chemical bonding, and thermodynamics) are given more gradual development than before. Others, such as electron descriptions, solid-state chemistry, and reaction mechanisms, have been extended closer to present practice. Descriptive chemistry has been reemphasized with expansion in some areas (e.g., silicates) and compression in others (e.g., noble gases). Completely new topics (e.g., wave functions, symmetry, molecular vibrations, and chain reactions) have been introduced. Much of the discussion is quantitative; it has been made more quantitative, both in breadth and depth.

The book is divided into three parts—Part I develops the principal concepts of chemistry; Part II applies these concepts to a systematic survey of the characteristic behavior of the chemical elements; Part III synthesizes the principles and properties into a critical overview of chemical limitations on the quality of life. Although the assumption has been made that the student begins with a rudimentary knowledge of chemistry, it is not assumed that he or she is headed for a career in chemistry. Rather, the principles established and the descriptive chemistry used as illustrations are broadly based so as to be appropriate as well for the engineer, the medical student, the agronomist, and the molecular biologist.

The general arrangement of Part I is that of increasing complexity—atoms, molecules, states of matter, solutions, reactions, equilibrium. However, should an instructor wish, he can start with Chapter 5 on states of matter and then go back to Chapter 1 or 2, depending on the sophistication level of his class. A few of the sections (i.e., 2.2, 3.10, and 7.2) have fine-print parts that are more difficult but can be omitted without loss of continuity. Some calculus is introduced, but only gradually and sparingly, and then only where needed. Numerous worked-out problems are included in the body of the text. Extended lists of exercises (over 800 in all, all new for this edition) are appended to each chapter. Each list of exercises is presented in order of increasing difficulty, culminating with a challenge for even the best of students. Numerical answers have been furnished for about half the problems; the remaining answers as well as worked-out solutions are included in an instructor's manual available from the publisher.

The second part of the book deals intensively with the elements of the periodic table. While all the elements are covered, emphasis is on the elements that are typical, those that constitute important resources, and those that are important in life and in materials science. Hydrogen, oxygen, and water are given special treatment; they are followed by group discussion from left to right across the table. The transition elements are considered in detail, first in general and then individually. Organic chemistry appears in depth but not in breadth, mainly as an interesting and unusual aspect of carbon chemistry. Equilibrium computations and thermodynamic applications are used repeatedly in the second half of the book, especially in the problem sets at the ends of chapters. Because qualitative analysis is still one of the best ways to learn solution chemistry and is often the vehicle for much laboratory work of the second semester, there has been included considerable information for detection of the common elements.

Part III is an entirely new part of the book which examines the special problems of man in his chemical environment. Air, water, food, and pollution are considered inputs for man; drugs and radiation are then treated as perturbing influences; finally, the problem of limits to growth is explored.

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In the writing of this revision, the recommendations of the International Committee on Weights and Measures and the International Union of Pure and Applied Chemistry (IUPAC) have been largely followed, particularly as regards the consistent use of SI (Système International) units and the sign convention for electrode potentials. Complete use of SI units was not feasible for practical reasons, e.g., most chemists do not use all SI units and would not even recognize some of them. Exotic ones such as *pascal* and *siemens* have not been adopted yet, and commonly accepted alternatives are still widely preferred. In a few instances, where pro-SI and anti-SI forces are at a standoff, we have leaned in the direction of SI. Consequently, we have adopted joule rather than calorie for the energy unit and mole rather than gram-atom for amount of chemical material. Atmospheres have been retained for pressure units; Torr has been eliminated. A complete discussion of SI units, together with recommendations and a list of equivalents, is given in an extensive appendix. The sign of the reduction potential has been adopted throughout for electrode potentials.

In the previous edition we concluded with a chapter on nuclear chemistry with a final optimistic note on the probability of unlocking nuclear fusion for the good of mankind. We end here with a less optimistic view of the unsolved chemical problems of man in his environment. Teaching freshman chemistry has always been a challenging assignment; with the present generation it needs more than ever to be "like it is."

The invaluable guidance and assistance of Professor John P. Hunt, Florence Bernard, and Barbara Zabadal in the preparation of this edition is gratefully acknowledged. Professor R. E. Hughes is to be thanked for the X-ray photograph of $RbMmF_3$ used in Figure 7.2.

Michell J. Sienko

Robert A. Plane

Contents

Preface *ix*

Part I Principles of Chemistry

Chapter 1 ***The Atom (I)*** *3*
Early Atomic Theory. Atomic Weight. Periodicity in Chemical Behavior. Experiments on the Electric Nature of Atoms. Atomic Spectroscopy. Discovery of the Nucleus. The Bohr Atom. Buildup of Atoms on Bohr Model.

Chapter 2 ***The Atom (II)*** *47*
Wave Nature of the Electron. Wave Functions. Electron Spin. Quantum Numbers and Orbital Filling. Many-electron Atoms. Atomic Radii. Ionization Potential. Electron Affinity.

Chapter 3 ***The Molecule*** *79*
Electrons in Molecules. Ionic Bonds. Covalent Bonds. Polarity of Bonds. Electronegativity. Bond Energies and the Scale of Electronegativity. Resonance. Shapes of Molecules and Hybrid Orbitals. Molecular Orbitals. Wave Functions of Molecules. Molecular Vibrations. Symmetry.

Chapter 4 ***Stoichiometry*** *126*
Moles of Atoms. Simplest Formulas. Molecular Formulas. Formula Weights and Molecular Weights. Chemical Reactions. Oxidation Numbers. Oxidation-Reduction. Balancing Chemical Equations. Calculations Using Chemical Equations. Equivalents.

Chapter 5 ***The Gaseous State*** *156*
Volume. Temperature. Pressure. *P-V* Relation. *V-T* Relation. Partial Pressures. Avogadro Principle. Equation of State. Graham's Law of Diffusion. Kinetic Theory. Kinetic Theory and Equation of State. Deviations from Ideal Behavior. Critical Temperature. Cooling by Expansion.

Chapter 6 ***The Liquid State*** *183*
Properties of Liquids. Equilibrium Vapor Pressure. Boiling Points. Surface Tension. Viscosity.

Chapter 7 ***The Solid State and Changes of State*** *196*
Properties of Solids. Determination of Structure. Space Lattice. Packing of Atoms. Solid-state Defects. Bonding in Solids. Crystal Energies. Heating Curves. Cooling Curves. Supercooling. Solid-Gas Equilibrium. Phase Diagrams. Entropy, Free Energy, and Spontaneous Change.

Chapter 8 ***Solutions*** *228*
Types of Solutions. Concentration. Properties of Solutions. Electrolytes. Percent Dissociation. Interionic Attractions. Solubility. Colloids. Light Scattering and Brownian Motion. Adsorption.

Chapter 9 ***Solution Reactions*** *258*
Acids and Bases. Neutralization. Polyprotic Acids. Hydrolysis. Amphoterism. Stoichiometry of Solutions.

Chapter 10 ***Chemical Kinetics*** *279*
Nature of Reactants. Concentration of Reactants. Temperature. Catalysis. Collision Theory. Stepwise Reactions. Chain Reactions. Energy Diagrams. Reactions in Aqueous Solutions. Very Fast Reactions.

Chapter 11 ***Chemical Equilibrium*** *311*
The Equilibrium State. Mass Action. Equilibrium Constant. Equilibrium Calculations. Heterogeneous Equilibrium. Equilibrium Changes.

Chapter 12 ***Equilibrium: Aqueous Solutions*** *332*
Dissociation. Calculations Using K_{diss}. Dissociation of Water; pH. Titration and Indicators. Buffer Solutions. Complex Ions. Solubility of Ionic Solids. Precipitation. Simultaneous Equilibria. Hydrolysis.

Chapter 13 ***Chemical Thermodynamics*** *365*
Systems and Functions. First Law. Enthalpy and Heat Capacity. Enthalpy Changes in Chemical Reactions. Second Law. Standard Free-energy Changes. Chemical Activities and Chemical Equilibrium. Temperature and Chemical Equilibrium.

Chapter 14 ***Electrochemistry*** *387*
Electric Conductivity. Electrolysis. Quantitative Aspects of Electrolysis. Galvanic Cells. Fuel Cells. Electrode Potentials. Nernst Equation. Free Energy and Cell Voltage.

Part II Properties of the Elements and Their Compounds

Chapter 15 ***Hydrogen, Oxygen, and Water*** *415*
Occurrence of Hydrogen. Preparation of Hydrogen. Properties and Uses of Hydrogen. Compounds of Hydrogen. Hydrogen Bond. Iso-

topes of Hydrogen. Proton Magnetic Resonance. Occurrence of Oxygen. Preparation of Oxygen. Properties and Uses of Oxygen. Compounds of Oxygen. Water. Water as a Solvent. Hydrates.

Chapter 16 ***Alkali and Alkaline-earth Metals*** *445*
Metallic Properties. Ion Species and Electrode Potentials. Occurrence of the Elements. Preparation of the Elements. Properties and Uses. Compounds of the Alkali Elements. Compounds of the Alkaline-earth Elements. Hard Water. Ion Exchange. Qualitative Analysis.

Chapter 17 ***Transition Elements I: General Aspects*** *472*
Electronic Configuration. Metallic Properties. Oxidation States. Ligand-Field Theory. Magnetic Properties. Spectral Properties. Complex Ions.

Chapter 18 ***Transition Elements II:* Sc, Ti, V, Cr, *and* Mn *Subgroups*** *491*
Scandium Subgroup. Lanthanides. Actinides. Titanium Subgroup. Vanadium Subgroup. Chromium Subgroup. Manganese Subgroup. Qualitative Analysis.

Chapter 19 ***Transition Elements III: Iron-Triad and Platinum Metals*** *516*
Iron Triad. Iron. Compounds of Iron. Corrosion of Iron. Cobalt and Nickel. Light Platinum Triad. Heavy Platinum Triad. Qualitative Analysis.

Chapter 20 ***Transition Elements IV: Copper and Zinc Subgroups*** *536*
Copper Subgroup. Copper. Silver. Gold. Zinc Subgroup. Zinc. Cadmium. Mercury. Mercury in the Environment. Qualitative Analysis.

Chapter 21 ***Group III Elements*** *561*
Group Properties. Boron. Aluminum. Gallium. Indium. Thallium. Qualitative Analysis.

Chapter 22 ***Group IV Elements*** *575*
Group Properties. Carbon. Compounds of Carbon. Hydrocarbons and Derivatives. Organic Reactions. Silicon. Germanium. Tin. Lead. Qualitative Analysis.

Chapter 23 ***Group V Elements*** *609*
Group Properties. Nitrogen. Phosphorus. Arsenic. Antimony. Bismuth. Qualitative Analysis.

Chapter 24 ***Group VI Elements*** *632*
Group Properties. Sulfur. Selenium. Tellurium. Polonium. Qualitative Analysis.

Chapter 25 ***Group VII Elements*** *647*
Group Properties. Fluorine. Noble-gas Compounds. Chlorine. Bromine. Iodine. Astatine. Interhalogen Compounds. Qualitative Analysis.

Part III *Man and His Chemical Environment*

Chapter 26 ***Air, Water, Food*** *669*
Pollutants in the Atmosphere. Internal-combustion Engine. Photochemical Smog. Octane Dilemma. Control of Air Pollution. Odors. Water Pollution. Detergents and Eutrophication. Chemistry of Flavor. Food Additives. Carcinogens. Insecticides.

Chapter 27 ***Drugs and Radiation*** *709*
Drugs. Drug Action. Morphine. Marihuana. LSD. Radiation Hazards in the Environment. Nuclear Energy, Reactors, and Bombs.

Chapter 28 ***Limits to Growth*** *735*
Resource Depletion. Energy Crisis. Limits to Growth.

Appendices

Appendix 1 ***SI Units.*** *744*

Appendix 2 ***Chemical Nomenclature. Inorganic Compounds. Organic Compounds.*** *747*

Appendix 3 ***Vapor Pressure of Water.*** *752*

Appendix 4 ***Mathematical Operations.*** *753*
Exponential Numbers. Logarithms. Quadratic Equations. Solving Equations by Successive Approximations.

Appendix 5 ***Definitions from Physics.*** *759*
Velocity and Acceleration. Force and Mass. Momentum and Impulse; Angular Momentum. Work and Energy. Electric Charge and Electric Field. Voltage and Capacitance. Electric Current.

Appendix 6 ***Dissociation Constants K_c and Solubility Products K_{sp}.*** *746*

Appendix 7 ***Standard Electrode Potentials.*** *766*

Appendix 8 ***Atomic and Ionic Radii.*** *769*

Appendix 9 ***References.*** *771*

Index *773*

Acquisition of knowledge is simplified by seeking basic principles. In chemistry, the principles include the generalizing statements that summarize observed phenomena and the theories that are proposed to account for the observations. Recognition of the principles of chemistry increases the depth of understanding and serves as a convenient framework for remembering a large body of information and also as a firm basis from which to make predictions about the unknown.

Principles of chemistry

Part I

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The atom (I) Chapter 1

Man has long speculated that matter in its ultimate state of subdivision is atomic—that it consists of discrete, indivisible particles. Early in the nineteenth century this idea was given quantitative expression by John Dalton. Working with the observed facts that in chemical reactions mass is conserved (law of conservation of matter) and that the combining ratio of elements is fixed by the compound formed, not by the available masses of starting elements (law of definite composition), Dalton was able to assign a self-consistent set of masses to the atoms of the various elements. Further, he was able to predict that if more than one compound is formed between two elements, the mass ratio of elements in one compound is a simple multiple of the mass ratio in the other compound (law of multiple proportions). We now know that none of the three aforementioned laws is precisely true; however, Dalton's idea of an indivisible, definite-mass atom persisted for almost a century and served as a most fruitful concept for the planning and execution of countless chemical experiments. The facts discovered, particularly that chemical properties varied in periodic fashion with increasing elemental atomic weight (the so-called "periodic law"), strongly hinted at an underlying structure for a divisible atom. The nature of this structure and how it has been deduced is the subject matter of this chapter.

1.1 *Early atomic theory*

The idea of an atom as an ultimate building block of matter appears to have originated with the early Greek philosophers. Two schools of thought were in lively contention: One believed that progressive subdivision of any sample of matter could be continued indefinitely; the other, that the process of subdivision had an ultimate limit. In the first view, even the smallest portion of a sample of matter is continuous, a sort of jelly that could be cut up into ever smaller and smaller regions, each being still jellylike in its consistency. The atomists, on the other hand, believed that any sample of matter is ultimately discontinuous. The process of chopping it up into bits would have to stop when it reached the ultimate, indivisible particles. These particles were called *atoms*, after the Greek word *ατομοσ*, *atomos*, meaning "indivisible."

Although very curious about the nature of their physical world, the Greek philosophers were not schooled to resort to controlled experimentation as a way to decide between conflicting theories. Also, their measuring instruments were too crude to deal with so subtle a concept as the atom. It remained for John Dalton to make the concept quantitative and apply it to an understanding of what matter is composed of and how it changes in the course of a chemical reaction. Although the idea of an atom as an ultimate building block has been very fruitful, it is not without ambiguity. In the modern view, the atom is believed to be composed of more "fundamental" units (e.g., protons, neutrons, and electrons), but the way these are held together or apart is not completely understood. Furthermore, the spatial extent of the assemblage of protons, neutrons, and electrons is not a clearly defined constant but depends on what else there is in the immediate environment. In particular, when two or more atoms "interact" with each other to form the more complicated unit we call a *molecule*, the distinct identity of the individual atoms is no longer retained; for many purposes, it is more useful to think in terms of the new unit formed. Still, we speak of the molecule as being composed of atoms, and the atom remains a useful, approximate concept that ties together a large body of observed behavior.

The Greek philosopher Empedocles taught in 440 B.C. that all matter is composed of four simple substances: earth, air, water, and fire. Aristotle, about 100 years later, replaced the concept of component elementary substances by "blendings" of abstract properties (e.g., coldness, hotness, dryness, and moistness). Robert Boyle, Irish chemist and physicist, writing in 1661 what was probably the first chemistry textbook, "The Sceptical Chymist," rejected the aristotelian view and gave the first modern definition of elements as "primitive and simple unmingled bodies which, not being made of any other bodies or of one another, are the ingredients of which mixt bodies are immediately compounded and into which they are ultimately resolved." By 1803, when Dalton proposed his atomic theory, approximately 10,000 compounds had been discovered; these were resolvable into about 35 elements, some of which, such as lime, subsequently proved to be com-

Name	Symbol	Mass, m_{e^-}	Charge, e
Electron	e^-	1	−1
Proton	p	1836	+1
Neutron	n	1839	0
Omega hyperon	Ω^-	3279	−1
Xi hyperon	Ξ	2586	−1
Sigma hyperon	Σ^-	2341	−1
Lambda hyperon	Λ°	2182	0
K meson	K°	974	0
Pi meson	π^+	275	+1
Muon	μ^-	208	−1
Neutrino	ν	<0.0005	0

Fig. 1.1
Some elementary particles.

pound in character. (The comparable modern figures are approximately 1 million compounds and slightly more than 100 elements.)

For his atomic theory of matter, Dalton made what amounts to the following assumptions: (1) All matter is ultimately composed of atoms. (2) Atoms can be neither subdivided nor changed one into another. (3) Atoms can be neither created nor destroyed. (4) Atoms of a particular element are identical with each other in size, shape, mass, and other properties; they differ from atoms of other elements in these properties. (5) Chemical change is the union or separation of undivided atoms.

Each of the above assumptions eventually proved to be wrong. For example, J. J. Thomson in 1897 showed that a common constituent of all atoms is a more elementary particle called the *electron.* It has a mass of 9.1096×10^{-28} g and an electric charge of -1.6022×10^{-19} coulomb. (Units and conversion factors are discussed in Appendix 1.) Subsequent work showed that atoms are composed of two other constituent particles: protons and neutrons. Although chemists in general now regard atoms as being composed only of electrons, neutrons, and protons, the actual situation is certainly more complicated. Figure 1.1 lists so-called "elementary particles" that have been obtained on the breakup of the atom. In the list, the masses of the particles are given as multiples of the electron mass; the charges are given in units based on the electron charge as −1.

Particle accelerators (e.g., the cyclotron and synchrotron) have enabled man to accelerate particles to such high energy that beams of energetic particles can be used to disrupt the fundamental forces holding the atom together. The daltonian atom has been chipped, split, smashed, and reassembled in anything but an indivisible manner. Fortunately for chemistry, most of the perturbation of atomic structure is of the chipping variety; so the great bulk of the atom remains recognizably unchanged in the course of a chemical transformation.

Dalton's key assumption that all the atoms of a given element are alike was shown to be incorrect by the discovery in 1907 of isotopes by H. N. McCoy and W. H. Ross. Isotopes, which are almost chemically inseparable from each other, have identical electronic makeups but differ from each other in mass because of subtle differences in the heart of the atom. The word *isotope* comes from the Greek *ισος* (same) and *τοπος* (place); it refers to the fact that isotopes occur in the same place when the chemical elements are arranged in a regular array according to their properties. For most chemical purposes, the existence of these isotopes can be ignored. Any collection of atoms such as encountered in chemical reactions can be characterized by an "average" atom which has a mass determined by the weighted mean of the various isotopes present. The principal effect of having identical atoms differing only in mass is to change the rate at which chemical transformations occur. For example, in the case of the element hydrogen, which is composed of three isotopes (protium, deuterium, and tritium), the lightest isotope generally undergoes chemical reaction most rapidly.

The final flaw of the Dalton theory was to assume that atoms remain unchanged in the course of a chemical reaction. This immediately ran into trouble because it begged the question of how atoms are able to stick together, either to their own kind or to atoms of a different kind. There followed an interesting period during which atoms were sometimes endowed with hooks and other mysterious "valence forces" to account for their combining capacity. At present, we know that rather minor electric modifications in the exterior reaches of an atom can explain why one atom binds to another; even so, we shall see that a simple particle picture will not suffice to account for chemical binding.

1.2 Atomic weight

The great concept that came out of the Dalton theory is that atoms can be characterized by their atomic weight. In this respect, we might note that we should be talking here about *mass,* not *weight.* What is the difference? Mass is an intrinsic inertial property, independent of the frame of reference. It measures the inertia of an object, i.e., its tendency to stay at rest or to continue in straight-line motion. Weight, on the other hand, is a force ($F = ma$; see Appendix 5.2) and tells how the object is being attracted in a given environment. An astronaut who has a weight of 70 kg on the face of the earth has a weight of zero in an orbiting satellite and a weight of 12 kg on the face of the moon. The gravitational pull is different in the three environments; his weight changes. However, his mass is the same in the three places. To push him away from another astronaut in the three environments would require the same effort for the same acceleration.

What about atoms? Strictly speaking, we would have to say that the atomic weight of a hydrogen atom, or any other atom for that matter, is zero in an orbiting satellite. Atomic-weight tables would then be meaningless. Actually they are not meaningless because we really are talking about atomic mass. So why not use "atomic mass" instead of "atomic weight"? There are two good reasons: For one thing, the term "atomic weight" and the related term "molecular weight" are so firmly ingrained in chemists' vocabularies that one needs to use them to communicate effectively. Secondly, the term "atomic mass" has taken on the connotation that it is the actual intrinsic mass of an individual atom that is meant. As chemists, we generally work with large numbers of atoms, and we need a relative number to describe an "average" atom in the collection. This relative number is based on reference to a given standard, currently the so-called "carbon-12" isotope of the element carbon. It is convenient to use atomic weight when referring to this relative number and to save atomic mass for referring to the absolute mass of an individual atom.

Dalton was the first to set up a scale of atomic weights for the elements. He chose as his reference the lightest element, hydrogen, and assigned it a value of unity on his arbitrary scale. Other elements were then given higher values depending on how much heavier their atoms were compared with hydrogen. To fix the relative weights, compounds were analyzed and their compositions as percent by weight used to apportion the distribution of mass. Unfortunately, Dalton made two mistakes: First, his analysis of water was faulty. On decomposing water into its component elements hydrogen and oxygen, he found 12.5% by weight hydrogen and 87.5% oxygen. (The true figures are 11.19% H and 88.81% O.)* He concluded that oxygen contributed seven times as much to the total weight as did the hydrogen. (He should have found eight times.) His second mistake was more serious. He assumed that a molecule of the compound water consisted of one atom each of hydrogen and oxygen. Since all the water molecules are alike, since all the hydrogen atoms are alike, and since all the oxygen atoms are alike, weight analysis of bulk water told him directly that the weight distribution in each water molecule is 1 part for the hydrogen and 7 parts for the oxygen. Hence the conclusion was that the atomic weight of oxygen is 7 units on a scale where hydrogen is 1. (In similar fashion he proceeded to examine other compounds where different elements were combined with oxygen. Having once decided that oxygen had an atomic weight of 7, the other elements could be assigned their appropriate values.) Actually, the water molecule contains *two* hydrogen atoms bound to a single oxygen atom. As a consequence, one-seventh of the mass of the water molecule has to be spread over two hydrogen atoms; each hydrogen atom contributes only one-fourteenth the total mass of the molecule. Had Dalton guessed the atomic makeup of water correctly, he would have had to assign a value of 14 for his atomic weight of oxygen. If we go further and correct his analysis result from one-seventh to one-eighth, we would get 16, a value which is not far from the presently accepted value, though the latter is based on quite a different method of assignment.

Shortly after the appearance of Dalton's list of atomic weights based

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* In most cases the symbol for an element is just the capitalized first letter of the name, for example, H for hydrogen, O for oxygen, and P for phosphorus. If several elements have the same initial letter, a second small letter may be included in the symbol, for example, He for helium, Ho for holmium, and Ha for hahnium. In some cases, particularly for elements known since antiquity, the symbols are derived from Latin names, for example, K from *kalium* for potassium, Fe from *ferrum* for iron, and Au from *aurum* for gold. Symbols for all the elements are given on the inside back cover of the book.

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