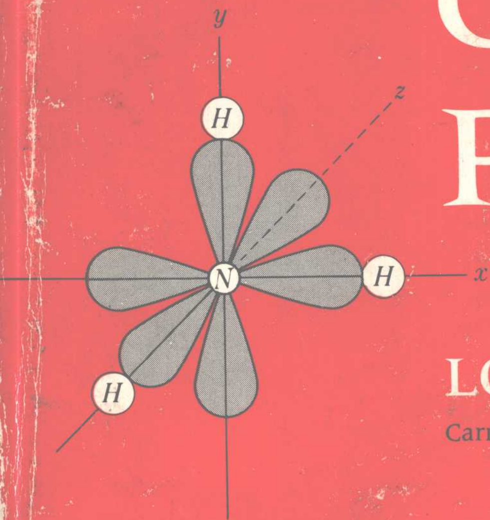
Chemical Principles



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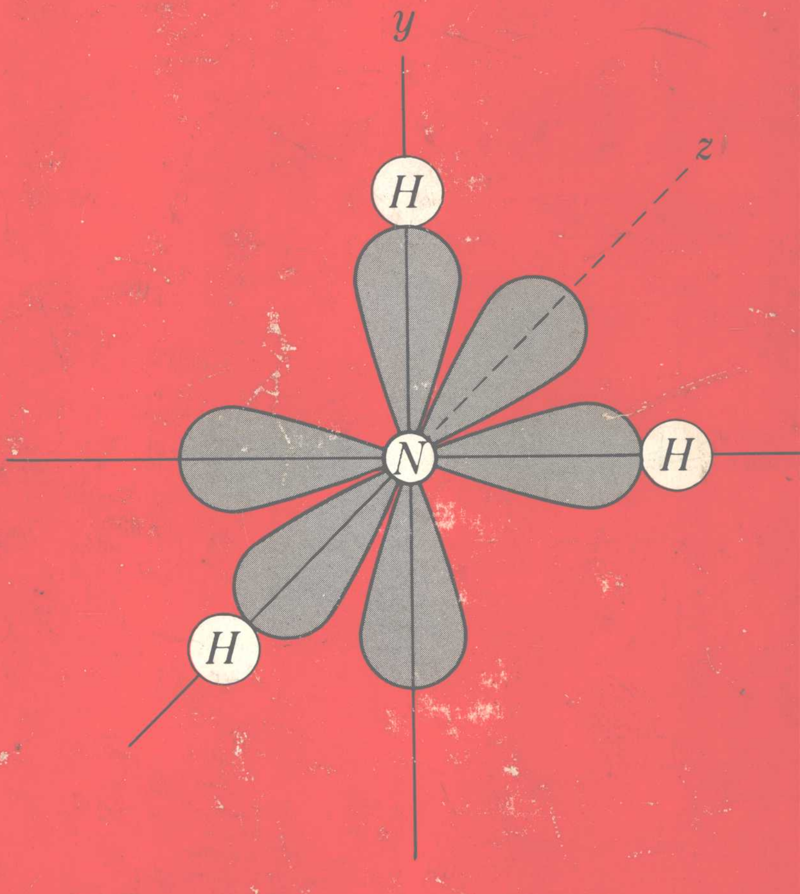

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Chemical Principles

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Chemical Principles

A Blaisdell Book in the Pure and Applied Sciences

PREFACE

Chemical Principles has been written primarily for a first year college course in chemistry for students who are seriously interested in science or engineering. It is my opinion that this course should include the following: (a) discussions of atomic and molecular structure and properties in terms of quantum theory, (b) chemical applications of thermodynamics, (c) study of chemical kinetics in terms of rate equations and reactions mechanisms and (d) selected reaction chemistry.

The study of chemical reactions should be tied in as much as possible with structural considerations and thermodynamics and it seems better to consider the chemistry of several elements in some detail than to pass lightly over all the elements. Some of the reaction chemistry of the common elements is described qualitatively. Still more reaction chemistry is given in terms of equilibrium constants, oxidation potentials, free energies and heats of reaction. Many chemical properties and reactions are interpreted in terms of electronic configurations, available orbitals, bond energies, lattice energies, hydration energies, etc. The relation of atomic structure to the arrangement of the elements in the periodic table is emphasized along with the use of the periodic table as an aid in learning and remembering chemical information.

Since chemistry is a big and growing subject, a satisfactory introduction to chemical principles and a systematic introduction to organic chemistry require much more time than is available in the course for which this book is intended. Therefore I have not attempted to include a traditional systematic introduction to organic chemistry. Although no chapter titled "Organic Chemistry" is included in this book, the book does contain quite a lot of information about organic compounds and their reactions. Various sections of the book are specifically concerned with structures, reactions or physical properties of certain groups of organic compounds. Many of the examples and problems involve organic compounds.

Most students learn chemistry best by solving problems, many of which should involve quantitative calculations. Many of the problems in this book have been designed for the conventional purpose of giving students practice and testing their ability to use their knowledge of chemical principles. Other problems are intended as introductions to material treated in detail later or as supplementary material for the best students. Answers to some of the problems are given in an Appendix.

Exponential notation, logarithms and simple algebra are used without apology, although every effort has been made to explain clearly what has been done. Beginning in Chapter 10, some simple calculus is used. Again, every effort has been made to explain the mathematical operations and the physical significance of these operations.

I am pleased to acknowledge my debt to my teachers at the Universities of Kansas and California and my students at the University of Virginia and the Carnegie Institute of Technology. Of the many students who have helped me, I especially thank Barbara Bashein for critically reading and typing about half of the final manuscript. Dorothy Ponsetto, Marilou Hrach and my wife have also helped by making copies of early drafts and by typing part of the final manuscript.

Many of my friends and colleagues have read parts of various drafts of the manuscript and have made valuable suggestions. I am grateful to all of these people and particularly thank Stanley Angrist, Henry Bent, Leo Brewer, Paul Fugassi, Robert L. Graham, Z Z. Hugus, Jr., Edward L. King, Gilbert Mains, John Margrave, R. Bruce Martin, William McMillan, Paul Schatz, Richard Stein and Bart van't Riet.

Loren G. Hepler

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CHAPTER 1

INTRODUCTION

LANGUAGE OF CHEMISTRY

A dictionary definition of chemistry is "the science that treats of the composition of substances, and of the transformations which they undergo." Various chemists and students have semi-facetiously defined chemistry as "what chemists do," but this definition is improperly restrictive because many non-chemists do some chemistry in the course of their other work and also make use of chemistry done by chemists. Since a complete definition of chemistry is certainly impractical and maybe impossible, we proceed in this book with an introduction to the scientific principles that form the foundations of modern chemistry.

The language of chemistry contains terms such as Mg, F_2 and H_2O. These letters sometimes are used as abbreviations for the substances magnesium, fluorine and water. These letters also are used as symbols to represent an atom of magnesium, a molecule of fluorine consisting of two fluorine atoms and a molecule of water consisting of two hydrogen atoms and one oxygen atom. In certain cases these same letters are used as symbols to represent a particular (6.02×10^{23}) large number of magnesium atoms, fluorine molecules or water molecules.

Water and many other substances exist in the solid (usually crystalline) state, the liquid state or the gaseous state at various temperatures and pressures. Chemists commonly write $H_2O(c)$, $H_2O(liq)$ and $H_2O(g)$ to represent crystalline water (*ice*), liquid water and gaseous water (*water vapor or steam*). Similarly, Fe(*c*), $CH_3OH(liq)$ and $N_2(g)$ represent crystalline iron, liquid methyl alcohol (wood alcohol) and gaseous nitrogen.

Some substances exist in more than one solid form. For instance, carbon can be in the form of graphite, diamond or in an amorphous, non-crystalline form. We write C(*gr*), C(*diamond*) and C(*amorph*) to represent carbon in these forms. Similarly, we write S(*rh*) and S(*mono*) to represent sulfur in the rhombic and monoclinic forms.

Many substances dissolve in water to form solutions that are discussed in detail in this book. To indicate that a substance is dissolved in water (*in aqueous solution*), we write (*aq*) after the symbol for the substance. Thus, $CH_3OH(aq)$ represents methyl alcohol in aqueous solution. We might also write $NaCl(aq)$ for ordinary table salt dissolved in water, but will usually write $Na^+(aq) + Cl^-(aq)$ to indicate that aqueous sodium chloride is dissociated into oppositely charged particles called ions. In general, we write chemical symbols, formulas and equations as realistically as possible and in such fashion as to convey as much information as possible.

In writing chemical equations to represent chemical reactions, we use the symbols $\rightarrow$ and $\rightleftharpoons$. For example, we might write

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(c)$$

for the reaction of gaseous ammonia with gaseous hydrogen chloride to yield crystalline ammonium chloride. Or we might write

$$NH_4Cl(c) \rightarrow NH_3(g) + HCl(g)$$

for the reaction that occurs on heating solid ammonium chloride. We might also write

$$NH_4Cl(c) \rightleftharpoons NH_3(g) + HCl(g)$$

when we are concerned with both the forward and reverse reactions as in the study of chemical equilibrium.

Physical processes are also represented by equations. We write

$$H_2O(c) \rightarrow H_2O(liq)$$

for the melting of ice, but we write

$$H_2O(c) \rightleftharpoons H_2O(liq)$$

when we are concerned with both the melting of ice and the freezing of liquid water or when we are concerned with ice and water in equilibrium as at 0°C and one atmosphere pressure.

The language of chemistry contains many words that are not commonly used in the non-scientific world or that are used differently in scientific and non-scientific connections. Formal and explicit definitions are given in this book for a few scientific terms, but for the most part the meanings of new words and expressions are illustrated by use and example rather than by definition.

MATHEMATICS

Numerical calculations form an important part of chemistry. These calculations involve the use of logarithms, determination of square roots and higher roots and arithmetical operations with both very large and very small numbers, as illustrated later in this section. The numbers in most chemical calculations represent definite physical quantities. Thus, when we mean to express a length or a mass, we write 10 cm or 5 gm rather than merely 10 or 5. Units (such as gm, cm, cal, etc.) have been included throughout most of the calculations in this book. In other calculations, insertion of units has been left as an exercise for the reader.

Algebraic rules for handling exponentials are the following:

(1) To multiply exponentials having the same base, add exponents.
(2) To divide exponentials having the same base, subtract the exponent of the divisor from the exponent of the dividend.
(3) To raise an exponential to a power, multiply the exponent by the power.
(4) To obtain the nth root of an exponential, divide the exponent by n.
(5) An exponential x^n equals $1/x^{-n}$; conversely, $x^{-n} = 1/x^n$.

Example Problem 1.1

Evaluate the following expression:

$$\frac{(3^{1.5})^2(3^2)(x^{14})(x^{-2})}{(3x^5)^2(x^2)}.$$

Application of Rule 3 to the first terms in the numerator and denominator and application of Rule 5 to the last term in the numerator give

$$\frac{(3^3)(3^2)(x^{14})}{(3^2)(x^{10})(x^2)(x^2)}.$$

Rules 1 and 2 now lead to $(3^3) = 27$ for the desired answer.

Example Problem 1.2

Evaluate the following expression:

$$\frac{10^{3.167} \times (10^{2.664})^{1/2}}{(10^{1.080})^{3/2}}.$$

We reduce the above expression to

$$\frac{10^{3.167} \times 10^{1.332}}{10^{1.620}}$$

and then to

$$10^{2.879}.$$

Handy tables (called logarithm tables) permit us to convert the exponential answer to the more convenient number 757.

Before proceeding with detailed discussion of the use of logarithms, we turn to the use of exponentials as a convenient means of expressing both very large and very small numbers. The number 4683 may be expressed as 4.683×1000 or as 4.683×10^3. Similarly, 602,000,000,000,000,000,000,000 is conveniently expressed as 6.02×10^{23}. The small number 0.00321 may be expressed as 3.21/1000, as $3.21/10^3$ or as 3.21×10^{-3}.

Example Problem 1.3

Evaluate the following expression:

$$\frac{[(3.12 \times 10^{-4}) - (5.6 \times 10^{-5})](1.27 \times 10^{3})}{(4.22 \times 10^{-2})^{2}(2.50 \times 10^{-3})^{1/2}}.$$

We first express 5.6×10^{-5} as 0.56×10^{-4}, which is then subtracted from 3.12×10^{-4} to yield 2.56×10^{-4}. Multiplying $2.56 \times 10^{-4} \times 1.27 \times 10^{3}$ gives 3.25×10^{-1} for the numerator of the expression above.

Squaring 4.22×10^{-2} gives 17.8×10^{-4} or 1.78×10^{-3}. We express 2.50×10^{-3} as 25.0×10^{-4}, and then take the square root to obtain 5.0×10^{-2}, which is multiplied by 1.78×10^{-3} to give 8.90×10^{-5} for the denominator.

Dividing the numerator by the denominator gives 3650.

Multiplication, division, determination of roots and raising numbers to a specified power are arithmetical operations that are conveniently carried out with the aid of logarithms. The common logarithm of a number is the power to which 10 must be raised to equal the number under consideration. Thus, the log of 1 is 0, the log of 10 is 1, the log of 100 is 2 and (by Rule 5 for handling exponentials) the log of 0.01 is -2. In general, the log of 10^{n} is n.

Logarithms of numbers that are not integral powers of 10 are customarily obtained from log tables or a slide rule. Since tables of logarithms list the exponents to which 10 must be raised to yield numbers between 1 and 10, we ordinarily express all numbers as numbers between 1 and 10 times the appropriate 10^{n}. Thus, we write 462.1 as 4.621×10^{2} and 0.0000387 as 3.87×10^{-5}. The log of 4.621 is listed in log tables as 0.6647, and the log of 10^{2} is 2. According to Rule 1 for handling exponentials, we add 0.6647 to 2 to obtain 2.6647 as the desired log of 4.621×10^{2}. Similarly, the log of 3.87 is 0.5877, and the log of 10^{-5} is -5. Adding 0.5877 to -5 gives -4.4123 as the log of 3.87×10^{-5}.

An antilog is the number to which a logarithm corresponds. For example, the antilog of 2 is 100. To find the antilog of 2.6647, we see in a log table that 4.621 is the antilog of 0.6647 and already know that 100 is the antilog of 2. Since $2.6647 = 2 + 0.6647$, we multiply 4.621×100 (or 4.621×10^{2}) to obtain the desired antilog of 2.6647.

To find the antilog of a negative log, we rewrite the negative log in the form of a positive number between 0 and 1 minus the appropriate integer. Thus, we write -4.4123 as $0.5877 - 5$. The antilog of 0.5877 is 3.87 and of -5 is 10^{-5}, so the antilog of -4.4123 is 3.87×10^{-5}.

Example Problem 1.4

Use logarithms to evaluate the following expression:

$$\left[\frac{5.12 \times 10^{-2} \times 6.42 \times 10^{4}}{3.62 \times 10^{-3}}\right]^{3/5}.$$