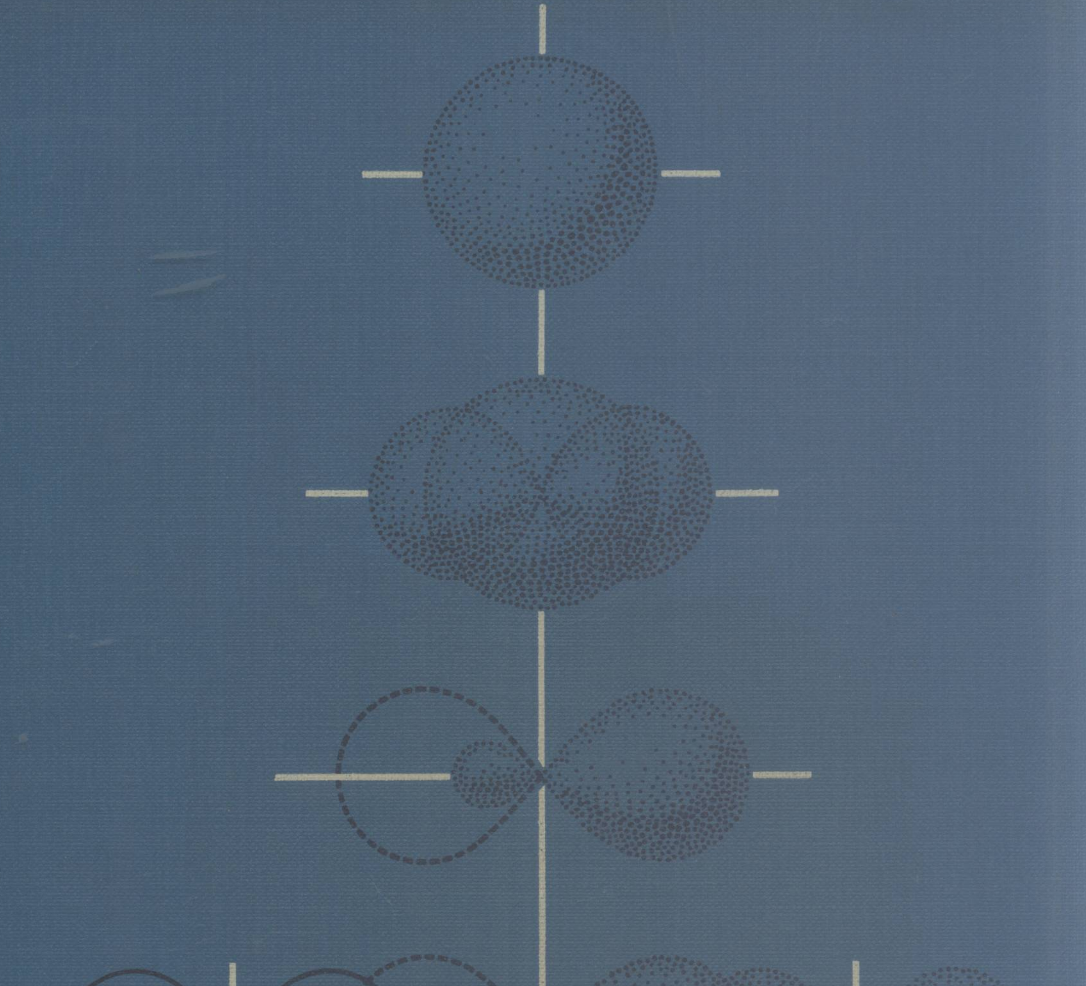

Chemistry

PERROS

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Chemistry

To Megalopolis in Arcadia,
and especially to Issari
from whence my mother and father came

Preface

That a course in introductory chemistry can concurrently fill the needs of a science major and challenge the nonscience major has been the author's guiding premise for this text. It assumes no previous experience in chemistry, nor does it require any knowledge of calculus. With supplementary readings, it may be used for honors courses.

Chemical principles have been developed from their origin to their current status, with excerpts from original reports often cited as part of the discussion. The aim is not only to show how and why principles evolve but to demonstrate that chemistry is a dynamic science, whose concepts, though valid today, may have to be discarded or modified tomorrow.

The importance of theory often can be best appreciated by demonstration of experimental data. Thus a balanced discussion of theoretical and descriptive chemistry is offered, with the descriptive element introduced at an early stage, integrating fundamental principles with experimental findings. The solution of sample problems has been used liberally to illustrate the application of principles.

The Valence Bond Theory is emphasized as the most easily understood concept to introduce the nature of the chemical bond. The Molecular Orbital Theory is cited briefly where appropriate in the text proper and is discussed further in Appendix 3. The concepts of entropy and free energy are developed to provide the student with the basic understanding needed for an ability to predict the direction of chemical reactions.

A concept is often applied in a functional manner to aid in the development of a specific principle and then discussed later in greater depth. In this way, the student may benefit by the greater understanding gained from reinforced repetition.

With the exception of hydrogen and oxygen, which have chapters of their own, the chemical elements are discussed by periodic groups. Trends with respect to properties, structure, and bonding within groups are stressed. The transition elements, the lanthanide and actinide elements, and the rare gases are treated with more than customary detail, with emphasis on the more recent developments. At the conclusion of the chapters dealing with the chemistry of the elements, a brief commentary describes their uses and economic importance.

In many chapters, particularly those dealing with the chemistry of the elements, the presentation has been organized to permit selective omission of sections and still allow the student to obtain an effective understanding of the properties of the elements.

To acknowledge everyone who assisted in the preparation of this text is impossible, but this does not lessen the gratitude. Special nods of thanks go to my colleagues, Dr. Charles R. Naeser, Dr. Benjamin Van Evera, Dr. Robert C. Vincent, Dr. David G. White, and Dr. Reuben E. Wood, for their constructive suggestions, and to Linda Davis and Dr. Sardul Singh, for their kindness in checking the problems. The patience and stamina of Mary-Franklin Guthrie for wading through the original manuscript and preparing a perfect typewritten copy requires recognition of the highest order.

THEODORE P. PERROS

Chemistry

"The inquiry of truth, which is the lovemaking or wooing of it; the knowledge of truth, which is the praise of it; and the belief of truth, which is the enjoying of it, is the sovereign good of human nature."

FRANCIS BACON
(1561–1626)

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Matter and Measurement

THE SCIENCE OF CHEMISTRY

The science of chemistry has its roots in antiquity, when empirical procedures for many processes were developed by the cut-and-try method. The extraction of metals from their minerals and the manufacture of alloys and glass had already reached a fairly high level of development. But during the early Christian era and throughout the Middle Ages, there were few advances in techniques and in the discovery of new processes. It was not until the Renaissance that men conducted experiments with appropriate concern for logical procedures. It was then, too, that the necessity of quantitative measurement for meaningful experiments became recognized.

Progress in chemistry in the latter part of the eighteenth and well into the nineteenth century was so great that this period is sometimes referred to as the Golden Age of Chemistry. The pace has not slackened, and today we find that chemistry pervades every facet of our lives. The areas of interest of chemistry are myriad and are only touched by citing the major branches of inorganic chemistry, organic chemistry, and physical chemistry. Though each of these areas has its own characteristics, fundamentally they are all concerned with a systematic study of matter: the determination of its properties and the changes which it undergoes.

MEASUREMENT

The Metric System

Chemistry is an experimental science, and experimental observations require, among other things, systems for the measurement of volume, mass, and temperature. It is not difficult to conceive how confusing it would be if every nation had a separate set of standards for making these measurements. Fortunately, a set of standards for length, mass, and volume established in France in 1796 and called the *metric system* has been accepted by almost all nations. The United States is the only major nation which has not officially adopted this system, and even here virtually all *scientific* measurements employ this system.

STANDARD OF LENGTH The standard unit of length is the meter. It has recently been redefined as equal to 1,650,763.73 wavelengths of the orange-red spectral line of the krypton isotope with mass 86. The meter was formerly defined as the distance between two lines on a platinum-iridium bar carefully preserved at Sèvres, near Paris. Copies of this standard were distributed to several countries to encourage use of the metric system. The National Bureau of Standards in Washington, D.C., possesses one of these copies. The new standard of length was adopted for several reasons, one being that small changes occur in the length of the metal bar as its temperature varies, whereas the spectrum of krypton is unaffected by temperature changes.

A meter is approximately 39.37 inches. It is divided into 10 decimeters (deci equals $\frac{1}{10}$), 100 centimeters (centi equals $\frac{1}{100}$), and 1,000 millimeters (milli equals $\frac{1}{1,000}$). Thus 1 meter (m) equals 10 decimeters (dm) equals 100 centimeters (cm) equals 1,000 millimeters (mm).

A useful fact to remember is that 1 inch equals 2.54 cm. Thus,

$$1 \text{ inch} = 0.0254\text{m} = 0.254 \text{ dm} = 2.54 \text{ cm} = 25.4 \text{ mm}$$

For large distances, the kilometer (kilo = 1,000) is used. Obviously, 1,000 m = 1 km.

STANDARD OF MASS The metric standard of mass is the kilogram, originally intended to be the mass of 1,000 cubic centimeters of water at 4° Celsius, the temperature at which the density of water is at its maximum. A platinum-iridium cylinder, also preserved at Sèvres, was constructed as the standard. A replica of this cylinder is kept at the Bureau of Standards.

The unit of mass is the gram, $\frac{1}{1,000}$ of a kilogram. Just as the meter is divided into smaller units, so is the gram. A gram is equivalent to 10 decigrams (dg), 100 centigrams (cg), or 1,000 milligrams (mg).

$$1 \text{ g} = 10 \text{ dg} = 100 \text{ cg} = 1000 \text{ mg}$$

A useful fact is that 1 avoirdupois ounce = 28.35 g = 283.5 dg = 2,835 cg = 28,350 mg.

The kilogram is used for larger quantities: 1000 grams = 1 kilogram (kg).

STANDARD OF VOLUME The standard of volume is the liter, the volume of 1,000 grams of water at 4° C (Celsius). Since a gram of water at 4° C was supposed to have a volume of one cubic centimeter (cc), 1,000 grams of water at that temperature should have a volume of 1,000 cc. But a slight error was made in the creation of the standard kilogram, so that in fact 1 liter = 1000.027 cc. This slight difference is ordinarily ignored, although it must be considered when accuracy is paramount. Throughout this text, the ml and the cc will be used interchangeably.

The liter is divided into 1,000 milliliters—that is, 1 liter (l) = 1,000 milliliters (ml). Deciliters and centiliters are not often employed. A useful equivalence to bear in mind is that 1 liter = 1.06 quarts.

A summary of some useful metric-English equivalents is shown in Table 1-1.

Table 1-1: METRIC-ENGLISH SYSTEM EQUIVALENTS

Length	Weight	Volume
1 meter = 1.094 yards	1 kilogram = 2.205 pounds	1 liter = 1.06 quarts
1 meter = 39.37 inches	453.6 grams = 1 pound	29.57 milliliters = 1 fluid ounce
2.54 cm = 1 inch	28.35 grams = 1 ounce	

Temperature

FAHRENHEIT AND CELSIUS SCALES A practical means of determining whether something is hotter or colder than the reference points of a specific temperature scale is to measure its temperature with a thermometer. For example, the United States Weather Bureau records daily weather temperatures on the Fahrenheit scale. Two physical characteristics of water, its freezing point (FP) and its boiling point (BP) at one atmosphere of pressure, are selected as the bases for this thermometric scale. The value 32° is assigned to the FP and 212° to the BP. The Celsius* scale also uses the FP and BP of water as its reference points, and assigns them the values 0° C and 100° C, respectively. In scientific work the Celsius and the Kelvin (Absolute) scales, described below, are used almost exclusively.

A comparison of the Fahrenheit and Celsius scales yields a useful relationship, which is illustrated in Figure 1-1. The difference between the BP and FP of water on the Celsius scale is 100; on the Fahrenheit scale it is 180. Thus for every 1° C change there is a $^{180}/_{100} = ^{9}/_{5} = 1.8°$ F change. To convert a Celsius reading to the Fahrenheit scale is a simple matter. For example, 30° C is equivalent to $^{9}/_{5} \times 30 = 54°$ F on the Fahrenheit scale; since the base for this scale (that is, the FP) is 32° F rather than 0° F, this value must be added

* Also referred to as the centigrade scale.

to 54° F to give the equivalent Fahrenheit temperature. This is written simply as:

$$
\begin{aligned}
°\,F &= (9/5)°\,C + 32\\
°\,F &= 9/5 \times 30 + 32\\
°\,F &= 54 + 32\\
&= 86
\end{aligned}
$$

The reverse reading (conversion of ° F to ° C) is easily obtained:

$$
\begin{aligned}
°\,F &= (9/5)°\,C + 32\\
(9/5)°\,C &= °\,F - 32\\
°\,C &= (5/9)\,(°\,F - 32)
\end{aligned}
$$

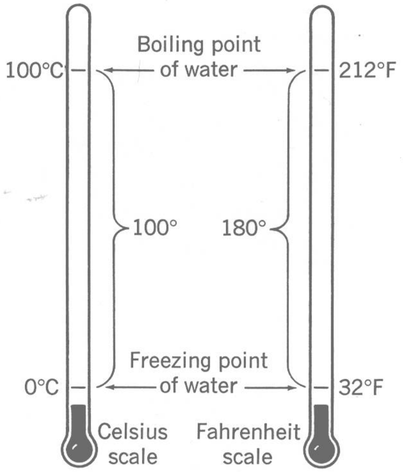

Figure 1-1 *Two temperature scales.*

$$\frac{(\text{B.P.} - \text{F.P.})\ °\text{F}}{(\text{B.P.} - \text{F.P.})\ °\text{C}} = \frac{180}{100} = \frac{9}{5} = 1.8$$

1 ° C change equals 1.8 ° F change.

THE KELVIN SCALE The Kelvin (Absolute) temperature scale is based on the uniform contraction or expansion of a confined gas as its temperature changes while its pressure is constant. This contraction or expansion has been found to be 1/273 of its 0° C volume per Celsius degree. Since the Kelvin degree is the same size as the Celsius degree, the Kelvin temperature (K) is obtained by adding 273 (more precisely, 273.15) to the Celsius reading. This can be written ° K = ° C + 273. The minimum reading on this scale is 0° K (−273° C). This is the lowest temperature attainable and is often referred to as absolute zero. Experiments have obtained temperatures a few hundredths of a degree above this limiting value.

Density and Specific Gravity

DENSITY The words *heavy* and *light* are often used to indicate the relative weight of objects in a very general sense. If one uses these words to compare objects whose sizes (volumes) are the same, one is actually describing a property of the objects. This property is called *density,* and it is defined as the mass per unit volume.

$$D = \frac{M}{V}$$

where

$$
\begin{aligned}
D &= \text{density of the substance}\\
M &= \text{mass of the substance}\\
V &= \text{volume of the substance}
\end{aligned}
$$

The densities of solids and liquids are usually given in units of grams per cubic centimeter: g/cc. Occasionally the densities of gases are given in units of g/ml, but since the densities of gases are rather small, they are more often expressed in units of grams/liter at a specified temperature and pressure.

Since temperature affects the volume of liquids and gases, it is obvious that densities vary with temperature. It is for this reason that density values are accompanied by the temperatures at which the determinations were made—for example, the density of mercury at 20° C is expressed as $D_{20} = 13.55$ g/cc. The densities of some familiar substances are given in Table 1-2.

Table 1-2: DENSITIES OF FAMILIAR SUBSTANCES AT 20° C

Aluminum	2.70	Silver	9.4
Copper	8.92	Sodium	0.93
Mercury	13.55	Starch	1.53
Platinum	21.45	Sucrose (sugar)	1.59
Potassium	0.83	Sulfur	2.07

SPECIFIC GRAVITY The specific gravity of a substance is the ratio of the weight of a given volume of the substance to the weight of an equal volume of another substance taken as a standard at stated temperatures. For solids and liquids, the standard is water and for gases the standard is air or hydrogen. This is a ratio, so that, in contrast with density, it has no units.

$$\text{Specific gravity} = \frac{\text{weight of volume of x}}{\text{weight of equal volume of standard}}$$

The values for specific gravity (sp. gr.) are noted in reference books in the following manner:

$$\text{sp. gr.} \frac{t_1}{t_2}$$

The notations t_1 and t_2 refer respectively to the temperatures of the substance and of the water at which the determinations were made. For example, the specific gravity of aluminum chloride may be given as

$$\text{sp. gr.} = 2.44 \frac{25^\circ}{4^\circ}$$

This means that the specific gravity of aluminum chloride at 25° C is 2.44 referred to water at 4° C. The values of the specific gravity and the density are equal only at 4° C, where the density of water is 1.00000 g/cc.

The specific gravity of a liquid is normally determined by the use of a small container called a *pycnometer*. This is filled with the liquid and weighed;

it is then emptied, dried, filled with water, and weighed again. Since the volume is constant, the ratio of the weights is the specific gravity.

For those instances in which the reference is to water not at 4° C but at other temperatures, the true density can be determined by multiplying the specific gravity by the density of water at that temperature. For example, the specific gravity of sodium chloride at 15° C is 2.49. This is recorded as

$$\text{sp. gr.} = 2.49^{15°}$$

The absence of a temperature reading underneath the 15° indicates that the value is referred to water at the same temperature. Table 1-3 lists the densities of water at selected temperatures, and we see that at 15° its density is 0.99913 g/ml.

Table 1-3: DENSITIES OF WATER AT SELECTED TEMPERATURES

Temp. ° C	Density g/ml
0	0.99987
4	1.00000
10	0.99973
15	0.99913
20	0.99823

For sodium chloride at 15° C, then,

$$\begin{aligned}\text{Density} &= 2.49 \times 0.99913 \text{ g/ml}\\ &= 2.48 \text{ g/ml}\end{aligned}$$

The specific gravity of gases is often measured with reference to air, which is assigned a specific gravity of 1.

Heat

SPECIFIC HEAT If we take one-gram samples of a variety of substances, place them separately into an insulated container, and heat each with an appropriate heating coil, we find that the quantity of heat necessary to raise the temperature of each one-gram sample by one degree Celsius is different for each substance. This phenomenon is due to a property of each substance called its *specific heat,* defined as the heat energy necessary to raise the temperature of one gram of the substance one degree Celsius.

CALORIE The calorie (cal.) is the amount of heat energy necessary to raise the temperature of one gram of water from 15° C to 16° C at standard