BRESCIA
ARENTS
MEISLICH
TURK

FUNDAMENTALS OF CHEMISTRY

FOURTH
EDITION

Fundamentals of Chemistry

FOURTH F ON

FRANK BRESCIA
JOHN ARENTS
HERBERT MEISLICH
AMOS TURK

The City College of the
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PREFACE

The fourth edition is an entirely new text.

We have addressed ourselves to the following oft-debated questions about introductory chemistry, and have provided, we hope, some novel approaches.

Question. **How should chemistry be introduced?** Should it start on the "high road"—atomic structure → chemical bonding → periodicity → stoichiometry and the mole → . . . ? Or is the "low road" the better choice—the quasi-historical approach that teaches molecular and atomic weights through the study of gases, then goes on to stoichiometry and the mole, and only later to atomic structure?

Our Answer. We go around more than once. An early introduction to the language and tools of the chemist makes everything else pedagogically more digestible. A "gentle" atomic structure is therefore presented very early, but there is more to come later. The gentle beginning prepares the student for atomic and molecular weights by mass spectrometry. Stoichiometry and the mole, gases, and an introduction (gentle, again) to solutions and molarity follow closely. This opening gambit also makes life easier in the laboratory, since the early material can serve as the background for many experiments. Thermochemistry and a more thorough treatment of atomic structure come next, and we are on our way.

Question. **What about descriptive chemistry—when, where, and how much?**

Our Answer. We start in what will probably be about the middle of the first semester, in the chapter on periodicity, where you will find a section on the descriptive chemistry of the elements. We have done our level best to make it interesting. More descriptive matter is integrated into various other chapters dealing with chemical principles, such as those on bonding, acids and bases, and electrochemistry. Still more appears as the major portion of various chapters—those on analysis of ions in solution, nuclear chemistry, transition elements, organic chemistry, and polymers. Finally, the chapter on environmental chemistry is a mine of descriptive chemistry, some old (such as the metallurgy of iron and aluminum), some new (such as the chemistry of pollution and of the ozone layer), as well as of other special topics, from which illustrative material can be extracted throughout the course. More than that, the chapter is a capstone to the entire year of general chemistry; it shows the student how the various topics of previous chapters coalesce into "one chemistry" that can be applied to practical chemical problems.

Question. **How should chemical bonding be treated?** Should classical and quantum mechanical approaches be presented consecutively, or should the more advanced treatment come later?

Our Answer. Each way has merit; each cause has many advocates. To make either choice possible, we offer a classical approach to chemical bonding that will appear during the first semester. A more sophisticated quantum mechanical treatment comes later in the book. However, the latter material can be taken up immediately after the introductory chapter by those who wish to do so.

Question. **How much thermodynamics (if any) should be taught in general chemistry?**†

Our Answer. We come down clearly on the side of thermodynamics. Though many of our readers will not become professional chemists, the majority are destined for other science-based vocations. All are destined to live in a science-based world. Many will never take a course in physical chemistry or in thermodynamics. We do not attempt to prove all of our thermodynamic equations, but we do provide physical explanations, which may be worth more than rigorous mathematical derivations. The first law comes early. We take a chemical rather than physical approach to entropy, which is introduced via the universal tendency toward disorder. Its relationship to heat comes later. The second law is stated both qualitatively and quantitatively. Free energy is also introduced, still in the relatively simple context of phase transitions. These ideas are then used in later chapters, especially those on chemical equilibrium, electrochemistry, kinetics, complex ions, and environmental chemistry.

Question. **How should a major new topic be introduced?** What is the best way out of the dilemma of presenting all the experimental evidence first (too much!) or of explaining the principles first ("handing down from above")?

Our Answer. We have again tried going around twice. This can be seen best in the study of gases and in the introductions to chemical bonding, to the properties of solutions, and to thermodynamics. First we describe a series of simple experiments that lead to insightful but qualitative answers. Then, on the second lap, the subject is explored in appropriate depth—with regard both to theory and experiment. Something of this approach is brought to bear in many other parts of the text as well.

The main complaint that students have against general chemistry is that it is episodic—a potpourri of different topics. Many do not see how chemistry "hangs together" until they take organic chemistry. In some measure they are right, but the separation is in the books and the classroom, not in the science. We have made every effort to give the student the sense of continuity that chemistry deserves.

The last half-dozen chapters suggest this continuity most effectively, and the instructor is encouraged to select as much from them as the schedule will allow.

"STUDENT WELFARE"

Aids to the student also include the following:

☐ A preamble for each chapter, which sets the stage and tells the student what to expect.
☐ More complete explanations, improved readability, and deletion of some special topics such as the Carnot cycle and *p-d* π-bonding.
☐ Many more worked-out examples in the text.
☐ Key words and learning objectives set out at the end of each chapter.
☐ A "self-test" for each chapter, which should be scored by the student. To this end, each question is assigned points adding up to 100%, and the answers are provided in the back of the book. The self-test surveys the essential material in the chapter.

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† See *J. Chem. Ed.* **56**, 522 (1979).

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☐ A large selection of homework problems, in addition to the self-test. These range from simple drills to rather thought-provoking problems, including everything in between. Answers to numerical problems are provided in the back of the book.

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TO THE STUDENT

There are many ways to study a textbook. However, we have incorporated into the text some special features that can help you, and you should take advantage of them. We suggest that you go over each chapter twice, first for a quick orientation, and second for more serious study, as follows:

First Round. Read the opening page, which sets the stage and tells you what to expect. Now scan the chapter attentively but quickly, so you can anticipate in more detail what you will be hearing in the lecture. Look at the worked-out examples, which will prepare you for the types of problems you will be assigned. At the end of the chapter the lists of key words and chapter objectives will reinforce this information. You will find it a great help to do all this *before* you attend your first lecture—the lecture will be much clearer to you as a result.

Second Round. You are ready for a serious study of the chapter. As you read it, pay special attention to the illustrative examples and try to solve each one before looking at the worked-out answer. Don't struggle for long with it—even a brief attempt will help you to understand the question better. Then go over the solution carefully, making sure you understand each step. When you have finished the chapter, do the self-test and score yourself. There is no time limit. The answers are in the back of the book.

You are now ready to work out the additional homework problems assigned by your instructor. Check your answers to the numerical problems with the answers in the back of the book. Do as many problems as you can. Think of what practice can do in a sport, in a performing art, or in a language skill. It does the same for chemistry.

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Chapter
1
SOME FUNDAMENTAL TOOLS OF CHEMISTRY

This chapter introduces some of the language of chemistry and emphasizes the units of measurement chemists use. Significant figures, conversion factors, and the meaning of precision and accuracy are then discussed. Finally, the concept of a pure substance is introduced.

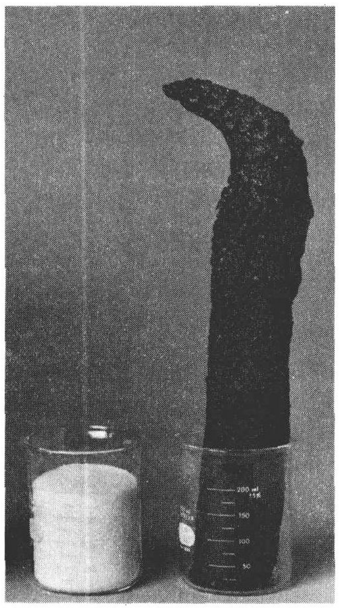
You may want to refer to the Appendix for reviews of physical concepts and mathematical procedures as well as the various tables of data.

1.1 SCIENTIFIC METHOD FOR CHEMISTS

Wherever you may be as you start to read this book—your room, the library, outdoors—look at the things that surround you. Most of them are items whose shape or construction has some particular function or some recognizable identity—a chair to sit on, a cup to drink from, a book to read, a rock that is interesting to look at. These things are **objects.** Now imagine that each of these objects were cut into little pieces: the chair then is no longer a chair but slivers of wood; the cup is granules of porcelain; the book is paper; the rock is coarse sand. Wood, porcelain, paper, sand—you no longer call them objects; they are **materials.** And materials are samples of **matter,** which is simply the stuff of which the universe consists.

Chemistry is the study of the properties and transformations of materials.

Now let us return to your cut-up objects. If you brought them all to a recycling center and disposed of them in the proper bins, you would put shredded books, shredded newspapers, and shredded milk cartons into the same bin, because you recognize that although they come from different objects, they are all of the same material, paper. Paper has some resemblance to wood, because they both can burn. And ground porcelain is a little like sand, because both contain hard grains of noncombustible matter. Thus by noting these resemblances, you have begun to classify materials. Classification therefore makes us recognize that different materials in the same class must have something in common. It might occur to you that the various materials observed have a complex inner structure, and are in fact combinations of simpler, more fundamental kinds of matter. By this reasoning, if two materials are similar, perhaps their resemblance results from the fact that they do indeed have some fundamental component in common.



Heating sugar in the absence of air produces carbon.

Such thoughts cry out for an experiment. You may at some time have gotten the impression that "scientific method" demands a sequence of steps that starts with "pure," unprejudiced observations and then progresses to hypothesis, theory, and finally scientific law. Alas, it is never so simple. In fact, a scientist who had no preconceived notions would simply have no idea as to what experiments to try. On the contrary, there is always a back-and-forth exchange between ideas and experiments.

Let us then think what might be done to put to test the thought that wood and paper, say, have some component in common. Suppose you shred each particle into smaller and smaller portions with the finest blade available. No luck—all you get is one pile of tiny fibers of paper and another of wood dust. Heating might be a better method. When a piece of paper is heated in the absence of air, it loses shape, chars, emits gases, and finally leaves a black residue, carbon. A similar procedure with the wood yields the same final product. The experiment thus confirms the idea that paper and wood have some material in common, namely carbon. Perhaps even more important, the results now suggest many other experiments; for example, do all things that burn contain carbon? We heat sugar and find that it does. Magnesium is also combustible, but heating magnesium in the absence of air just makes it get hot and melt. It does not produce any carbon nor any other new substances. The answer to the question "Do all things that burn contain carbon?" is *no*—one exception is sufficient to disprove the rule. But now our exchange between ideas and experiments suggests another thought: Is there a special class of substances, like magnesium and carbon, that cannot be decomposed but rather are the elemental building blocks out of which all other materials are compounded? Many experiments support this notion, and we call these nondecomposable substances **elements.**

A **substance** is a material that has a definite composition. The chemist often thinks of a substance as being a pure material (see Section 1.6).

TABLE 1.1 Sources of names of some elements

ELEMENT	SOURCE OF NAME
Uranium	The planet Uranus, which was the outermost known planet of the Solar System when uranium was the end of the series of known elements. (More distant planets and heavier elements have since been discovered, however.)
Mercury	Mercury, the messenger god, who is quick. The element is a shiny metal that is liquid at room temperature. It flows quickly and looks alive—hence its other name, *quicksilver*.
Curium; einsteinium; fermium	Marie Curie; Albert Einstein; Enrico Fermi
Francium; germanium; polonium	France; Germany; Poland
Berkelium; yttrium; ytterbium; erbium; terbium	Berkeley, California; all the others are from Ytterby, Sweden
Europium	Europe
Xenon	Greek, *xenos*, a stranger
Hydrogen	Greek, *hydor*, water; and *genēs*, producing

Symbols of some of the more common elements:

hydrogen	H
carbon	C
nitrogen	N
oxygen	O
fluorine	F
sodium	Na
magnesium	Mg
aluminum	Al
silicon	Si
sulfur	S
chlorine	Cl
iron	Fe

There are 105 known elements.† Their names refer to planets, ancient gods, modern scientists, countries, cities, continents, and various Greek or Latin meanings (Table 1.1). Each name is also denoted by a symbol of one or two letters, usually an abbreviation of the English name, but sometimes of the Latin one. The complete list appears inside the back cover.

Many chemical problems require solutions that are expressed in numerical terms. For example, you might want to know *how much* carbon is contained in a given weight of sugar, how hot the sugar must be in order to decompose, and how much time is required for the reaction to be completed. The answers to such questions can be obtained only by making *measurements*.

1.2
MEASUREMENT AND THE INTERNATIONAL SYSTEM OF UNITS

Imagine that you carried all of human knowledge in your head and that you visited another planet inhabited by beings similar to yourself. Your mission is to bring them the benefits of Earth's science (especially chemistry). Assume, however, that you had no measuring devices with you—no rulers, thermometers, standard weights—nothing. Would the mission be possible? Because science is overwhelmingly based on measurements, you would somehow have to duplicate the Earth's systems of measurement with whatever materials were at hand. We are confident that the chemical elements in other parts of the universe are the same as those we know here. (This confidence is based on overwhelming scientific evidence.) Let us then review our own system, and explore the question of its general utility.

The metric system was introduced as one of the radical innovations of the French Revolution in 1799. It spread gradually throughout most of the world, first to the scientific community and then to commerce and everyday life—except

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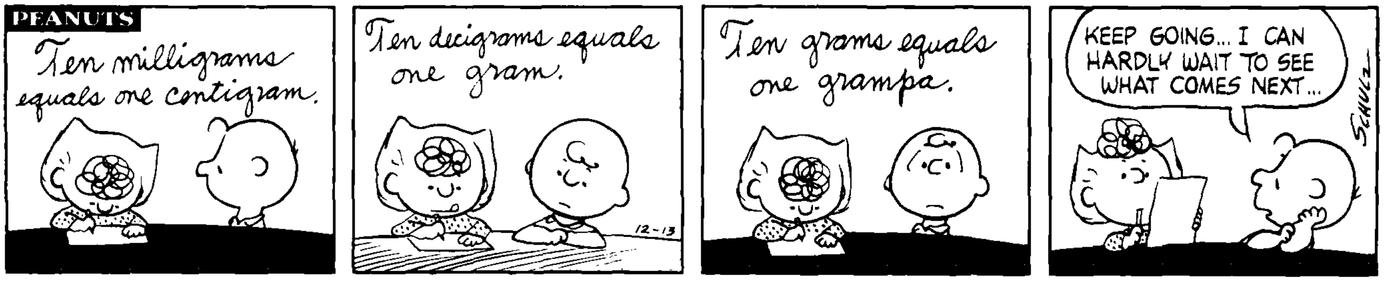
†This is the number of elements internationally accepted as of 1979. Discoveries of additional elements have been claimed but await international acceptance.


PEANUTS
Ten milligrams equals one centigram.
Ten decigrams equals one gram.
12-13
Ten grams equals one grampa.
KEEP GOING... I CAN HARDLY WAIT TO SEE WHAT COMES NEXT...
SCHULZ

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in the English-speaking countries, which are only now falling into line. It was established by an international treaty at the Metric Convention in Paris in 1875, and has since been extended and improved. The currently established official system is called the *International System of Units* (Système International d'Unités, abbreviated SI).

The International System has seven fundamental (base) units from which all others can be derived. The last one (the candela) is never referred to in this book; it is included just to complete the set. The base units are the following:

QUANTITY	UNIT	SYMBOL
Length	meter	m
Mass	kilogram	kg
Time	second	s
Temperature	kelvin	K
Electric current	ampere	A
Amount of substance	mole	mol
Luminous intensity	candela	cd

The SI rules specify that these symbols are not followed by periods nor are they changed in the plural. Therefore we write, "The beaker contains 5 g of mercury" (*not* "5 g. of mercury" or "5 gs of mercury"). The SI symbol for second, which is s, is often replaced by the unofficial sec, because an expression like 10 s is easily misread as tens. In this book we use sec for second.

Larger or smaller units in the SI are expressed by the prefixes shown in Table 1.2. Those from kilo, 10^3, to pico, 10^{-12}, are most commonly used by chemists.

TABLE 1.2 SI prefixes

MULTIPLE OR FRACTION	PREFIX	SYMBOL
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a

(μ is the Greek letter *mu*.)

EXAMPLE 1 How many (a) picograms in a milligram? (b) micrometers in a centimeter?

ANSWER (a) 10^{12} pg = 1 g and 10^3 mg = 1 g. Therefore

$$1\ \cancel{\text{mg}} \times \frac{1\ \cancel{\text{g}}}{10^3\ \cancel{\text{mg}}} \times \frac{10^{12}\ \text{pg}}{1\ \cancel{\text{g}}} = 10^9\ \text{pg}$$

Exponential notation is reviewed in Appendix B.2.

There are 10^9 or 1 billion picograms in a milligram.

(b) 10^2 cm = 1 m, and 10^6 μm = 1 m. Therefore

$$1\ \cancel{\text{cm}} \times \frac{1\ \cancel{\text{m}}}{10^2\ \cancel{\text{cm}}} \times \frac{10^6\ \mu\text{m}}{1\ \cancel{\text{m}}} = 10^4\ \mu\text{m}$$

There are 10^4 or 10,000 micrometers in a centimeter.

We now consider the first four base units listed above.

LENGTH The older metric standard was the distance between two lines on a platinum-iridium bar at the International Bureau of Weights and Measures in France. Of course, you could not duplicate this standard accurately unless you carried it with you, or at least carried another bar that had been measured against the original. However, since 1960 the meter has been defined as 1,650,763.73 times the wavelength of the orange-red radiation of the krypton-86 atom. It would therefore be possible for you to reproduce this anywhere, if you could get some krypton gas and had the necessary knowledge and skill.

Radiation from atoms is discussed in Chapter 7.

An older metric unit still in use is the ångstrom (Å). Some handy conversions are shown in Table 1.3.

Area (square meter) and volume (cubic meter) are derived units; hence no new standards are needed. For volume the SI also recognizes the **liter,** L, which is 10^{-3} m^3, or 1 dm^3. The liter was formerly defined as the volume of 1 kg of pure water at the temperature of its maximum density (3.98°C) at one standard atmosphere; however, this relationship, although still quite accurate, is not exact.

Because the liter is approved for use with the SI, so are its multiples and fractions, of which the most common is the milliliter, mL. One milliliter equals 1 cubic centimeter (cm^3).

The experimental setups for these measurements are not simple. You would need various materials to construct them.

TABLE 1.3 Conversions of some common units

1 ångstrom, Å = 10^{-10} m
= 10^{-8} cm
= 10^{-1} nm
1 in. = 0.0254 m
= 2.54 cm
1 *mi* = 1.609† km
1 m^3 = 10^3 L
1 L = 10^3 mL
= 1.057† quart (U.S., liquid)
1 ft^3 (U.S.) = 28.32† L
1 kg = 2.205† lb (avoirdupois)

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†These numbers are approximations to four significant figures. All other numbers are exact.

MASS The mass of a body is often said to be the quantity of matter it contains, although this is not much of a definition. To the physicist, the mass, m, is determined by the force, f, required to produce a given acceleration, a:

$$f = ma \quad \text{or} \quad m = \frac{f}{a}$$

Since force is also defined by this equation, the definition is rather circular and is not of much help on an imaginary planet. One experiment you could carry out, however, would be to expose two different bodies to the same acceleration, and if they exerted the same force, you could state that the two bodies have the same mass. When this experiment is carried out on Earth, the acceleration is determined by the Earth's gravity, and the procedure is called **weighing.** The two masses are said to be equal in weight when the forces they exert are equal. The only natural standards of mass are elementary particles like atoms, which are too small to be "weighed" with sufficient accuracy. Therefore the SI still relies on an artificial standard, that is, a piece of metal known as the Prototype Kilogram Number 1 (a platinum-iridium alloy). It is kept at the International Bureau of Weights and Measures, Sèvres, France. Consequently, there would be no way for you to make an exact reproduction on a strange planet. However, you could make a very good approximation based on the density of a known substance.

Density is mass per unit volume. The derived SI units are therefore kg/m^3, or the more familiar expression g/cm^3, which is the same as g/mL. The mass of ice-cold water needed to fill a 1.00-liter container is 1.00 kg. The density of ice-cold water is therefore 1.00 kg/L, or 1.00 g/mL, and you could duplicate the kilogram by using 1.00 liter of cold water.

More precisely, the density of water is 0.999973 g/mL at 3.98°C.

TIME The unit of time, the second, was originally defined as 1/86,400 of the mean solar day. Of course, this definition would do you no good away from Earth. Besides, the rotation of Earth is slightly irregular. In 1967 the second was redefined in terms of the frequency of a specific radiation from a particular atom (cesium-133). In any event, to duplicate the second exactly, you would have to obtain some cesium and some elaborate laboratory apparatus.

Frequency is the reciprocal of time; the unit is 1/sec, or sec^{-1}. One second is the duration of 92,631,770 cycles of the cesium-133 radiation.

TEMPERATURE Boiling water would feel hot if you dipped your finger in it, because heat flows from the water to your skin. The boiling water is said to be at a higher temperature than your finger. Conversely, an ice cube feels cold to the touch because heat flows from you to the ice; the ice is therefore at a lower temperature than your finger. **Temperature** is thus the property of a body that determines the direction of heat flow. The higher the temperature, the greater the tendency for heat to flow away from the body.

Many properties of substances change with changes in temperature. Examples are density, color, ability to conduct electricity, and ability to stimulate nerve impulses. A set of values in which temperature is related to some measured property is called a **temperature scale.** A device used to obtain such measurements is a **thermometer** (Figure 1.1).

The standard unit of temperature is the **kelvin** (symbol K, formerly called the "degree Kelvin," symbol °K). The temperature at which water, ice, and water vapor exist together at equilibrium serves as the reference point. This temperature, called the **triple point of water,** is assigned the exact value of 273.16 K.

The triple point of water is discussed in Chapter 11.

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