

FOURTH EDITION

CHEMICAL PRINCIPLES

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PREFACE

While working for the past two years on the fourth edition of *Chemical Principles*, we have frequently been asked, “Why revise a successful text?” There are many answers to this question, some more honest than others. Our objective has been to improve what has always been a student-oriented book, hopefully making it clearer and more interesting than its predecessors. We have been guided primarily by reactions from large numbers of college freshmen who have used the third edition. Included among these are the wife and son of one of the authors; their candid (occasionally caustic) suggestions about arguments that needed clarification have been particularly helpful.

We have also been influenced by the changing composition of the student body in general chemistry. Very few of our students are chemistry majors—most of them are preparing for careers in engineering, the biological sciences, medicine, and allied professions. They are not interested in abstract theory; instead, they want to know how the principles of chemistry can be applied to their field of interest and, more generally, to the world around them. With this in mind, we have consistently blended fact with theory, emphasizing the application of principles rather than their derivation. The environmental flavor of the third edition has been revised to include discussions of such topics of current interest as the energy crisis (Chapter 4) and the broader problem of the depletion of natural resources (Chapter 7).

The basic framework and sequence of topics common to previous editions have been retained. As before, introductory chapters (1–5) emphasize the quantitative, experimental aspects of chemistry. Descriptive inorganic chemistry is again organized around types of reactions (precipitation reactions in Chapter 18, acid-base reactions in Chapters 19 and 20, complex-ion formation in Chapter 21, and redox reactions in Chapters 22 and 23). Three chapters are essentially new: Chapter 7 (Periodic Table), Chapter 10 (Introduction to Organic Chemistry), and Chapter 25 (Natural and Synthetic Polymers). One effect of these additions is to increase somewhat the amount of descriptive chemistry relative to theory.

Those chapters which deal mainly with chemical principles have been reviewed for clarity and simplicity of argument. The discussion of thermochemistry in Chapter 4, which caused difficulties in earlier editions, has been completely

rewritten (several times!). Less extensive but significant changes have been made in the areas of electronic structure (Chapter 6), chemical bonding (Chapter 8), gaseous equilibrium (Chapter 15), and chemical kinetics (Chapter 16). Virtually all of the problems are new. The "historical perspectives," a popular feature of the third edition, have been expanded to include brief sketches of G. N. Lewis and Michael Faraday.

Several features are new in the fourth edition. The most immediately apparent is the series of color plates which appears in the center of the book. For these we are indebted to Ray Boyington and Ruven Smith, a pair of amateur but (by their own admission) talented photographers. Included for the first time in this edition, at the back of the book, is a glossary of chemical terms used throughout the text. At the end of each chapter, we have added a few particularly straightforward problems, each illustrating a single principle. We suggest that students, immediately after reading a chapter, work these problems to test their understanding of the material covered. Later, they can proceed to the other problems in the set, which are of the "matched pair" type used in the third edition.

Every author of a chemistry text nowadays has to decide how far to go in the use of the International System of Units. Regardless of how one feels about the merits of this system, it seems very unlikely that it will be adopted in the United States in the near future. For this reason we have not attempted to use SI units exclusively in this edition. Thus, we ordinarily use the calorie rather than the joule as an energy unit and the atmosphere rather than the pascal as a unit of pressure. However, this text is now available in an alternate version entitled *Chemical Principles, 4th Edition, SI Version*, where the International System is used consistently throughout.

A variety of supplementary materials are available for use with this text. Those which are new with this edition include:

Student's Guide to Chemical Principles, by Raymond Boyington and W. L. Masterton, which includes chapter summaries, self-tests, and basic skills sections.

Keller Plan for Self-Paced Study with Chemical Principles, by Joseph L. Clouser.

Workbook for General Chemistry with Audio-Tape Lessons, by B. K. Shakhshiri.

Modern Descriptive Chemistry, by Eugene Rochow, a short (250-page) paperback for those instructors who desire more material on the properties and reactions of the elements.

It is a pleasure to acknowledge the contributions to this edition by our colleagues at Macalester College and the University of Connecticut. Special recognition is due Chic Waring, whose many comments about content and organization are always appreciated and frequently followed. We are grateful to Jon Bellama of the University of Maryland, Clark Bricker of the University of Kansas, Bill Fisher of Clayton Junior College, Curt Sears of Georgia State University, Conrad Stanitski of Randolph Macon College, and Ted Williams of the College of Wooster, all of whom provided us with detailed, down-to-earth critiques of the third edition, and to Andy Ternay, University of Texas, Arlington; Ed Mellon, Florida State University; John Chandler, University of Massachusetts, Amherst; Grover Willis, California State University, Chico; Peter Berlow, Dawson College, Canada; and Carl von Frankenberg, University of Delaware. Joe Wiebush of the Naval

Academy, who went over the manuscript for this edition, is our all-time favorite among reviewers: brief and flattering. Finally, we should acknowledge the many contributions of the staff of the W. B. Saunders Company and, in particular, of our editor, John Vondeling. We are indebted to John for his unlimited energy, limited patience, and modest skill as a fly fisherman.

WILLIAM L. MASTERTON

EMIL J. SLOWINSKI

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CHEMISTRY: AN EXPERIMENTAL SCIENCE

Throughout all of history, the very existence of human life has been threatened by natural disasters, among them famine and disease. The degree of success achieved in our continuing struggle against such calamities is due in no small part to contributions from chemistry. During World War I, a German chemist, Fritz Haber, developed a practical process for the conversion of atmospheric nitrogen into ammonia, a principal component of the synthetic fertilizers now used to provide food for the world's expanding population. A generation later, another chemical, DDT, was used successfully to control malaria and other infectious diseases in war-ravaged areas of Asia and Europe. Since World War II, DDT and other chemical insecticides have been applied to increase agricultural production throughout the world.

In recent years we have become aware of some of the undesirable side-effects of chemicals developed to meet the needs of society. Chemical fertilizers promote the growth of algae that clog many of our lakes and streams. Pesticides such as DDT can have adverse effects on wildlife and, in some cases, on human life as well. In a more general sense, we have come to realize that the quality of our environment is threatened by materials produced in an attempt to achieve "a better life." Now we find that efforts to clear up our air and water are restricted by another, potentially catastrophic problem: the depletion of our natural resources. The "energy crisis" of the 1970's is only one indication of the fact that we are running out of the cheap raw materials upon which our economy is based.

Chemists, along with other scientists, are deeply involved in efforts to find solutions to the problems caused by pollution and dwindling resources. The sophisticated instruments used to measure pollutants in automobile exhaust at the part per million level were developed and applied by analytical chemists. Inorganic chemists were involved in the research that produced the "catalytic converters" now used to reduce harmful emissions from automobiles. Organic chemists, along with biochemists and biologists, have synthesized a variety of products that open up new approaches to the control of harmful insects. The search for new energy sources is being carried out by physical chemists working with physicists and engineers.

The approaches used by chemists and other scientists in solving problems are varied. Many significant discoveries have come about partly by chance. A biologist studying media for growing bacteria may accidentally contaminate his culture and thereby find a new antibiotic. A chemist studying the mechanism of a particular reaction may get a clue about a good catalyst for a very different reaction. Such discoveries cannot be attributed to luck alone; they require a mental attitude that

Chemistry deals with the properties and reactions of the materials which make up the earth and the universe.

is conducive to new ideas and an experimental environment in which they can be tested rigorously.

Regardless of how a new idea is generated, the method of testing it is one that has been used with considerable success in all the sciences for perhaps 200 years. The so-called “scientific method” starts with carefully designed experiments carried out in the laboratory under closely controlled conditions. Ordinarily, the system that a chemist works with is a relatively simple one, consisting perhaps of a single pure substance or a solution containing two or three such substances. Measurements on these systems, when properly interpreted, can lead to conclusions applicable to the more complex world that exists outside the laboratory.

In this beginning course in chemistry, we will discuss a great many different experiments. Many of these you will carry out in the laboratory; others you will have to visualize as they are described in the text or by your instructor. We will be interested in the principles or “laws” that can be developed from these experiments and in the application of these chemical principles to practical problems. In this chapter we will consider some very simple experiments that chemists carry out to identify pure substances and separate them from one another. Before doing so, it will be helpful to review the types of measurements that are fundamental to all experiments.

1.1 MEASUREMENTS

Most of the experiments carried out in chemistry laboratories are quantitative in nature. That is, they involve assigning numbers to such quantities as length, volume, mass, and temperature. We will now consider the instruments used to measure these quantities and the various units in which they may be expressed.

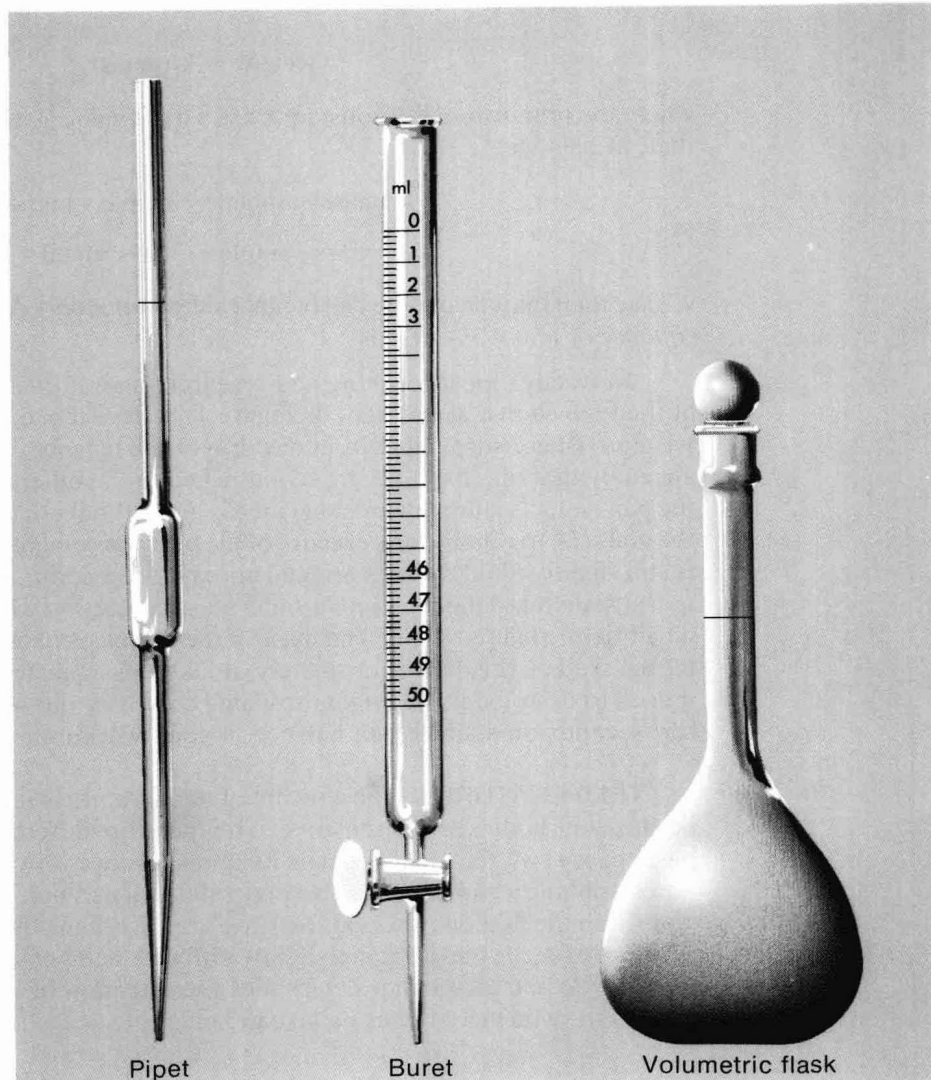
Measuring Devices

LENGTH. Most of us are familiar with a simple measuring device found in the general chemistry laboratory, the meter stick, which reproduces, as accurately as possible, the fundamental unit of length in the metric system, the **meter**. When we examine a meter stick, we see that it is divided into one hundred equal parts, each one *centimeter* in length ($1\text{ cm} = 10^{-2}\text{ m}$). A centimeter is, in turn, subdivided into ten equal parts, each one *millimeter* long ($1\text{ mm} = 10^{-3}\text{ m}$). A much larger unit, familiar to track and field runners, is the *kilometer* ($1\text{ km} = 10^3\text{ m}$). The prefixes “kilo,” “centi,” and “milli” are used in the metric system to designate units obtained by multiplying by 1000, 0.01, and 0.001 respectively. Two other units frequently used in chemistry to express the dimensions of tiny particles such as atoms and molecules are the angstrom ($1\text{ \AA} = 10^{-8}\text{ cm}$) and the nanometer ($1\text{ nm} = 10^{-9}\text{ m} = 10^{-7}\text{ cm}$).

VOLUME. Units of volume in the metric system are simply related to those of length. The cubic centimeter (cc or cm^3) represents the volume of a cube one centimeter on an edge. A larger unit is the liter, which was redefined in 1960 to be exactly 1000 cc; a milliliter has a volume exactly equal to that of one cubic centimeter.

The device most frequently used to measure volumes in the general chemistry laboratory is the graduated cylinder. When greater accuracy is required, we use a pipet or buret (Fig. 1.1). A pipet is calibrated to deliver a fixed volume of liquid (e.g., $25.00 \pm 0.01\text{ cm}^3$) when filled to the mark and allowed to drain normally. Variable volumes can be delivered with about the same accuracy from a buret.

Figure 1.1 Instruments used with liquids to deliver a fixed volume (pipet), deliver a variable volume (buret), or contain a fixed volume (volumetric flask). On the buret the numerical markings from 4 to 45 ml have been omitted.



Here, the final and initial readings must be made carefully to calculate the volume of liquid withdrawn. The volumetric flask shown at the right of Figure 1.1 is designed to contain a specified volume of liquid (e.g., 50, 100, . . . 1000 cm³) when filled to a level marked on the narrow neck.

Volumetric flasks are often used to prepare solutions to a desired concentration.

MASS. The amount of matter in a sample, its *mass*, is most frequently expressed in the metric system in *grams*, kilograms (1 kg = 10³ g), or milligrams (1 mg = 10⁻³ g). In the chemistry laboratory, mass is ordinarily measured by means of a balance (Fig. 1.2). To understand what is involved, consider the simple two pan balance shown at the left of the figure. We will assume that it has been adjusted so that, with nothing on either pan, the balance comes to rest with the two pans at the same height. To weigh an object, we place it on the left-hand pan. Metal weights of known mass are then added to the right-hand pan to restore balance, i.e., to bring the pans to the same height. Under these conditions, the gravitational force acting on the sample, its *weight*, is equal to that acting on the pieces of metal.

$$\text{weight sample} = \text{weight metal}$$

But Newton's first law of motion tells us that gravitational force is directly proportional to mass

$$\text{weight} = k (\text{mass}) \quad (1.1)$$

where the proportionality constant k has a fixed value at a given location. It follows that, at balance,

$$k (\text{mass sample}) = k (\text{mass metal})$$

or

$$\text{mass sample} = \text{mass metal}$$

We see then that the double pan balance detects not only *equality of weight* but also *equality of mass*.

Nowadays most teaching and research laboratories use single pan balances of the type shown at the right of Figure 1.2. Here a pan (A) and a set of movable weights (B) are suspended from one arm of the balance; their mass is exactly balanced by that of a fixed weight (C) attached to the other arm. Adding a sample to the pan deflects it downwards; balance is almost, but not quite, restored by turning the dials (D) to remove one or more of the movable weights. At this point, the beam is still slightly tilted from its original horizontal position. An optical system is used to translate this deflection into a small mass correction which appears as a number on a brightly lighted scale. The mass of the sample is obtained by adding this mass to that read on the dials. Fortunately, it takes less time to use this instrument than it does to describe it. Beginning students can carry out weighings to ± 0.001 g in a few seconds on a single pan balance in good working order.

TEMPERATURE. The concept of temperature is familiar to all of us, largely because our bodies are so sensitive to temperature differences. When we pick up a piece of ice, we feel cold because its temperature is lower than that of our hand. After drinking a cup of coffee, we may refer to it as "hot," "lukewarm," or "atrocious"; in the first two cases at least, we are describing the extent to which its temperature exceeds ours. From a slightly different point of view, temperature may be regarded as the factor that determines the direction of heat flow. Anyone brave enough to swim in a Minnesota lake in January feels cold because heat is absorbed

Single pan balances used in general chemistry weigh to ± 0.001 g or better; they should *not* be used for crude weighings

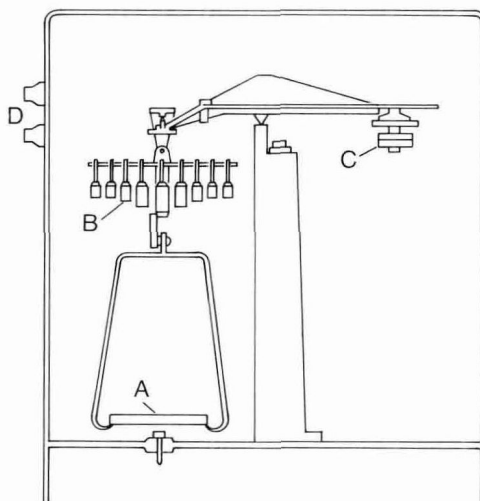
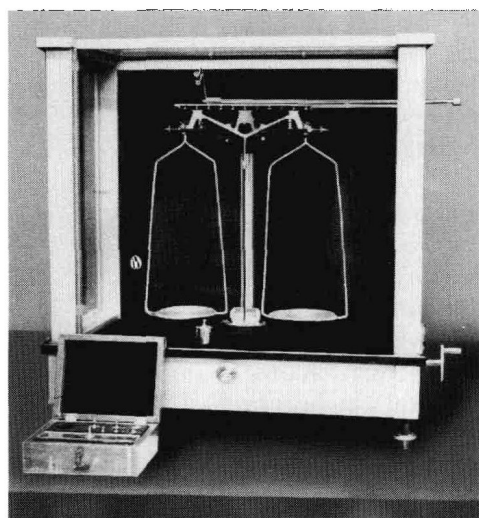
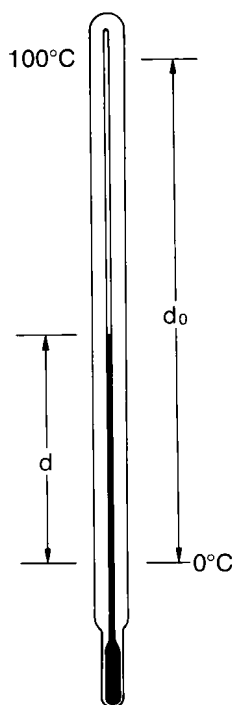


Figure 1.2 Two pan balance and schematic drawing of single pan balance. In most single pan balances, the weights are hung from the same frame that holds the balance pan. When a sample is put on the pan, weights are removed until balance is restored. With this design the balance works under a constant load.

Figure 1.3 At 45°C, as read on a mercury-in-glass thermometer, d equals 0.45 d_0 , where d_0 is the distance from the mercury level at 0°C to the level at 100°C.



from his body. If he takes a hot shower afterward, which he certainly will, heat flows in the reverse direction. In general, whenever two objects at different temperatures come in contact with each other, heat flows spontaneously from the higher to the lower temperature.

To measure temperature with a mercury-in-glass thermometer, we take advantage of the fact that mercury, like other substances, expands as the temperature rises. The thermometer is designed so as to make readily visible a rather small fractional change in volume (Fig. 1.3). The total volume of the thin capillary column is only about 2 to 3 per cent of that of the mercury reservoir at the base.

Thermometers used in the chemistry laboratory are marked in degrees Celsius (centigrade) after the Swedish astronomer, Anders Celsius (1701–1744). On this scale, the freezing point of water is taken to be 0°C and the boiling point at one atmosphere pressure to be 100°C. When we place a good quality mercury-in-glass thermometer in a beaker containing crushed ice in equilibrium with water, the mercury will come to rest exactly at the 0° mark. In a beaker of boiling water, the mercury will rise to the 100° mark. The distance between these two marks is divided as accurately as possible into one hundred equal parts, each of which corresponds to a Celsius degree. Thus, a temperature reading of 45°C corresponds to a mercury level 45 per cent of the way from the 0° mark to the 100° mark.

The Celsius scale is the common one in most countries

The common temperature scale used in the United States today is based on the work of Daniel Fahrenheit (1686–1736), a German instrument maker who was the first to use the mercury-in-glass thermometer. On this scale the normal freezing and boiling points of water are taken to be 32° and 212° respectively. This leads to a rather simple relationship between degrees Fahrenheit and degrees Celsius. From Figure 1.4 we see that °F is a linear function of °C. Since the equation of a straight line is $y = ax + b$, it follows that

$$^{\circ}\text{F} = a^{\circ}\text{C} + b$$

The constants a and b are readily evaluated; b is the intercept on the vertical axis, 32, while a is the slope of the line

$$a = \frac{\Delta y}{\Delta x} = \frac{212 - 32}{100 - 0} = \frac{180}{100} = 1.8$$

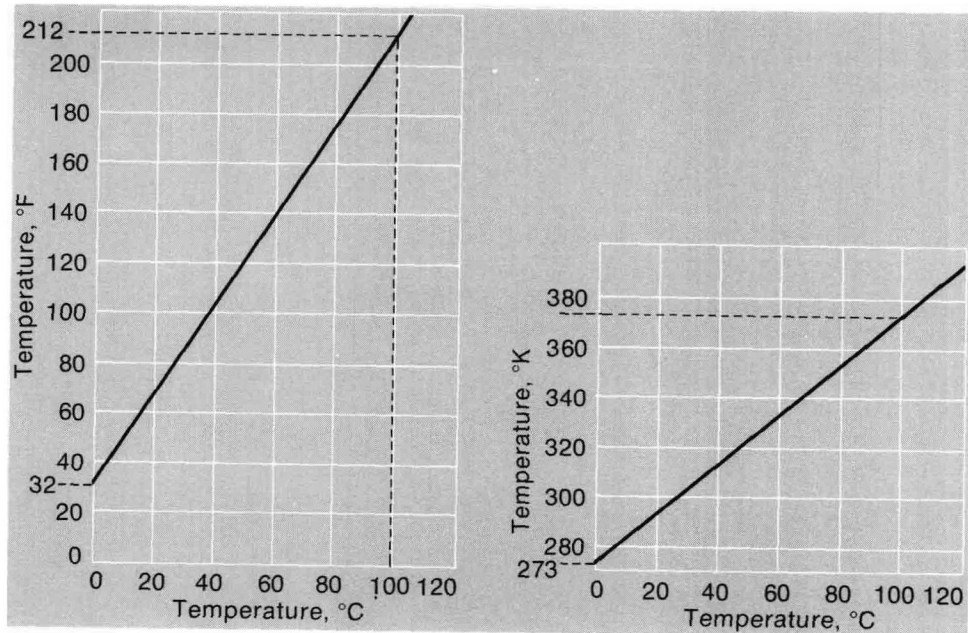


Figure 1.4 Relationship between two temperature scales. $^{\circ}\text{F} = 1.8^{\circ}\text{C} + 32$; slope is 1.8 and intercept is 32; $^{\circ}\text{K} = ^{\circ}\text{C} + 273$; slope is 1 and intercept is 273. The Celsius degree is equal in size to the Kelvin degree and is 1.8 times as large as the Fahrenheit degree.

Making these substitutions we obtain

$$^{\circ}\text{F} = 1.8^{\circ}\text{C} + 32 \quad (1.2)$$

Another temperature scale that we will find particularly useful in describing the behavior of gases is the absolute or Kelvin scale. The relation between $^{\circ}\text{K}$ and $^{\circ}\text{C}$ is

$$^{\circ}\text{K} = ^{\circ}\text{C} + 273 \quad (1.3)$$

Lord Kelvin, who entered college at the age of 10, was an old man of 26 when this work was published.

The scale is named after Lord Kelvin, an English physicist who demonstrated by a mathematical development based upon both theory and experiment that it is impossible to achieve a temperature lower than 0°K .

Example 1.1 Express normal body temperature, 98.6°F , in $^{\circ}\text{C}$ and $^{\circ}\text{K}$.

Solution Substituting in Equation 1.2, we obtain

$$98.6 = 1.8(^{\circ}\text{C}) + 32$$

Solving: $1.8(^{\circ}\text{C}) = 98.6 - 32 = 66.6$

$$^{\circ}\text{C} = 66.6/1.8 = 37.0$$

Applying Equation 1.3: $^{\circ}\text{K} = 37.0 + 273.0 = 310.0$

Uncertainties in Measurements: Significant Figures

Associated with every experimental measurement is a degree of uncertainty whose magnitude depends upon the nature of the measuring device and the skill with which it is used. If, for example, we attempt to measure out 8 ml of liquid using

a 100-ml graduated cylinder, the volume delivered is likely to be in error by at least 1 ml. With such a crude measuring device, we will be fortunate indeed to obtain a volume closer to 8 than to 7 or 9 ml. To improve on the accuracy of the measurement, we might use a narrow 10-ml cylinder on which the divisions are considerably farther apart. The volume we measure now may be within 0.1 ml of the desired value of 8 ml; i.e., in the range 7.9 to 8.1 ml. Using a buret, we might be able to do even better; if we are very careful, the uncertainty in our measurement may be reduced to 0.01 ml.

The person who carries out an experiment has a responsibility to indicate the uncertainty associated with his measurements. Such information is vital to anyone who wants to repeat the experiment or to judge its validity. There are many ways to do this; we might, for example, report the three volume measurements referred to above as

8 ± 1 ml	(large graduated cylinder)
8.0 ± 0.1 ml	(small graduated cylinder)
8.00 ± 0.01 ml	(buret)

Throughout this text, we will drop the \pm notation and simply write

8 ml; 8.0 ml; 8.00 ml

with the understanding that there is an *uncertainty of at least one unit in the last digit* (1 ml, 0.1 ml, 0.01 ml).

This method of specifying the degree of confidence in a measurement is often described in terms of **significant figures**. We say that in "8.00 ml" there are three significant figures; each of the three digits is experimentally meaningful. Similarly, there are two significant figures in "8.0 ml" and one significant figure in "8 ml."

Frequently we need to know the number of significant figures in a measurement reported by someone else. The manner in which this is deduced is illustrated in Example 1.2.

Example 1.2 An instructor asks his class in general chemistry to weigh a gold nugget. Among the masses reported are the following

20.03 g, 20.0 g, 0.02003 kg, and 20 g

How many significant figures should be assumed in each case?

Solution The student who reports 20.03 g clearly believes that each of the four digits is meaningful; he is specifying 4 significant figures. Similarly, the student reporting 20.0 g indicates 3 significant figures. She has placed the zero after the decimal point to make it clear that the nugget was weighed to the nearest 0.1 g.

A moment's reflection should convince you that the third student, like the first, has shown 4 significant figures. The zero immediately to the right of the decimal point is not significant; it is there only because the mass is expressed in kilograms rather than grams. By the same token, there are 2 significant figures in the quantity "0.064 g" and only 1 in "0.007 g."

We cannot be sure of the number of significant figures in "20 g." Perhaps the student weighed the nugget to the nearest gram and wants to indicate 2 significant figures. Then again he may be trying to tell us that his balance weighs only to the nearest 10 g, in which case only the first figure in "20 g" is significant. This ambiguity could be avoided by giving the mass in exponential notation (Appendix 4) as either

2.0×10^1 g; 2 significant figures

or

2×10^1 g; 1 significant figure

The number of significant figures in a measured quantity is equal to the number of digits shown when the quantity is expressed in exponential notation.