["The Experiment" by Sempe © C. Charillon, Paris.]

Quantitative Chemical Analysis

SEVENTH EDITION

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W. H. Freeman and Company
New York

Publisher: Craig Bleyer
Senior Acquisitions Editor: Jessica Fiorillo
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Illustration Coordinators: Shawn Churchman/Susan Timmins
Production Coordinator: Paul W. Rohloff
Composition: TechBooks/GTS Companies, York, PA
Printing and Binding: RR Donnelley

Library of Congress Control Number: 2006922923

ISBN-13: 978-0-7167-7041-1
ISBN-10: 0-7167-7041-5

Printed in the United States of America

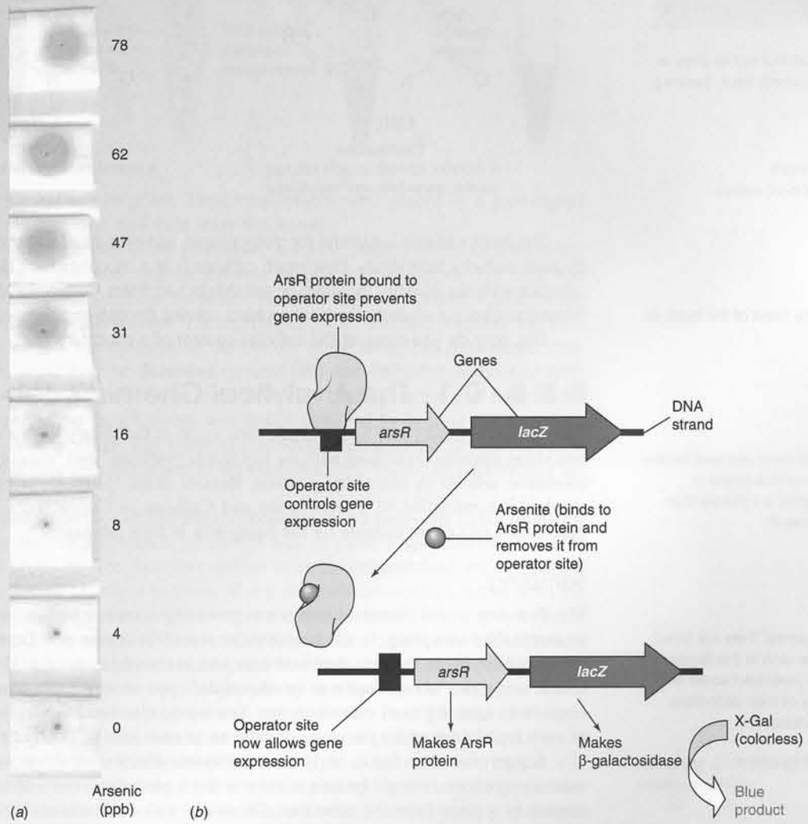
Fourth printing

W. H. Freeman and Company
41 Madison Avenue
New York, NY 10010
Houndmills, Basingstoke
RG21 6XS, England
www.whfreeman.com

Brief Contents

0 The Analytical Process

A BIOSENSOR FOR ARSENIC IN THE ENVIRONMENT[1,2]



(*a*) Test strips exposed to different levels of arsenite. *[Courtesy J. R. van der Meer, Université de Lausanne, Switzerland.]*
(*b*) How the genetically engineered DNA works.

In Bangladesh, 15–25% of the population is exposed to unsafe levels of arsenic in drinking water from aquifers in contact with arsenic-containing minerals. The analytical problem is to reliably and cheaply identify wells in which arsenic is above 50 parts per billion (ppb). Arsenic at this level causes vascular and skin diseases and cancer.

Panel (*a*) shows 8 test strips impregnated with genetically engineered *E. coli* bacteria whose genes are turned on by arsenite ($HAsO_3^{2-}$). When the strips are exposed to drinking water, a blue spot develops whose size increases with the concentration of arsenite in the water. By comparing the spot with a set of standards, we can estimate whether arsenic is above or below 50 ppb. We call the test strip a *biosensor,* because it uses biological components in its operation.

Panel (*b*) shows how the assay works. Genetically engineered DNA in *E. coli* contains the gene *arsR,* which encodes the regulatory protein ArsR, and the gene *lacZ,* which encodes the protein β-galactosidase. ArsR binds to regulatory sites on the gene to prevent DNA transcription. Arsenite causes ArsR to dissociate from the gene and the cell proceeds to manufacture both ArsR and β-galactosidase. Then β-galactosidase transforms a synthetic, colorless substance called X-Gal in the test strip into a blue product. The more arsenite, the more intense the color.

hocolate is great to eat, but not so easy to alyze. [W. H. Freeman photo by K. Bendo.]

diuretic makes you urinate.
vasodilator enlarges blood vessels.

otes and references are listed at the back of he book.

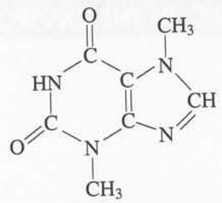
Chemical Abstracts is the most comprehensive ource for locating articles published in hemistry journals. *Scifinder* is software that accesses *Chemical Abstracts*.

Bold terms should be learned. They are listed at the end of the chapter and in the Glossary at the back of the book. *Italicized* words are less important, but many of their definitions are also found in the Glossary.

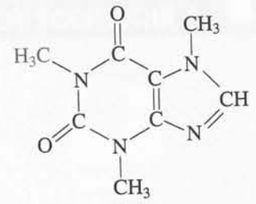
Homogeneous: same throughout

Heterogeneous: differs from region to region

Chocolate[3] has been the savior of many a student on the long night before a major assignment was due. My favorite chocolate bar, jammed with 33% fat and 47% sugar, propels me over mountains in California's Sierra Nevada. In addition to its high energy content, chocolate packs an extra punch with the stimulant caffeine and its biochemical precursor, theobromine.



Theobromine
A diuretic, smooth muscle relaxant, cardiac stimulant, and vasodilator



Caffeine
A central nervous system stimulant

Too much caffeine is harmful for many people, and even small amounts cannot be tolerated by some unlucky individuals. How much caffeine is in a chocolate bar? How does that amount compare with the quantity in coffee or soft drinks? At Bates College in Maine, Professor Tom Wenzel teaches his students chemical problem solving through questions such as these.[4]

But, how *do* you measure the caffeine content of a chocolate bar?

0-1 The Analytical Chemist's Job

Two students, Denby and Scott, began their quest at the library with a computer search for analytical methods. Searching with the key words "caffeine" and "chocolate," they uncovered numerous articles in chemistry journals. Reports titled "High Pressure Liquid Chromatographic Determination of Theobromine and Caffeine in Cocoa and Chocolate Products"[5] described a procedure suitable for the equipment in their laboratory.[6]

Sampling

The first step in any chemical analysis is procuring a representative sample to measure—a process called **sampling.** Is all chocolate the same? Of course not. Denby and Scott bought one chocolate bar in the neighborhood store and analyzed pieces of it. If you wanted to make broad statements about "caffeine in chocolate," you would need to analyze a variety of chocolates from different manufacturers. You would also need to measure multiple samples of each type to determine the range of caffeine in each kind of chocolate.

A pure chocolate bar is fairly **homogeneous,** which means that its composition is the same everywhere. It might be safe to assume that a piece from one end has the same caffeine content as a piece from the other end. Chocolate with a macadamia nut in the middle is an example of a **heterogeneous** material—one whose composition differs from place to place. The nut is different from the chocolate. To sample a heterogeneous material, you need to use a strategy different from that used to sample a homogeneous material. You would need to know the average mass of chocolate and the average mass of nuts in many candies. You would need to know the average caffeine content of the chocolate and of the macadamia nut (if it has any caffeine). Only then could you make a statement about the average caffeine content of macadamia chocolate.

Sample Preparation

The first step in the procedure calls for weighing out some chocolate and extracting fat from it by dissolving the fat in a hydrocarbon solvent. Fat needs to be removed because it would interfere with chromatography later in the analysis. Unfortunately, if you just shake a chunk of chocolate with solvent, extraction is not very effective, because the solvent has no access to the inside of the chocolate. So, our resourceful students sliced the chocolate into small bits and placed the pieces into a mortar and pestle (Figure 0-1), thinking they would grind the solid into small particles.

Imagine trying to grind chocolate! The solid is too soft to be ground. So Denby and Scott froze the mortar and pestle with its load of sliced chocolate. Once the chocolate

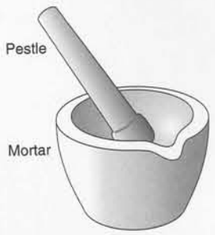


Figure 0-1 Ceramic mortar and pestle used to grind solids into fine powders.

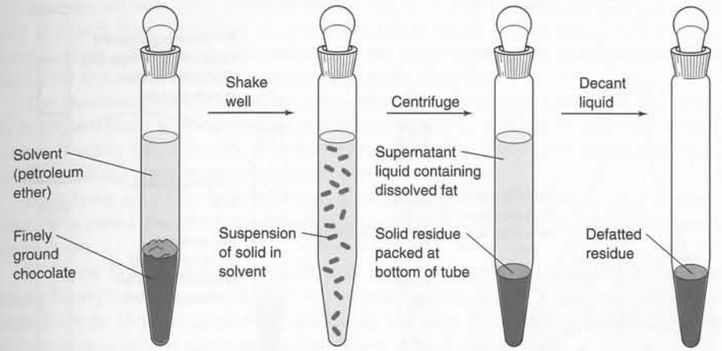


Figure 0-2 Extracting fat from chocolate to leave defatted solid residue for analysis.

was cold, it was brittle enough to grind. Then small pieces were placed in a preweighed 15-milliliter (mL) centrifuge tube, and their mass was noted.

Figure 0-2 shows the next part of the procedure. A 10-mL portion of the solvent, petroleum ether, was added to the tube, and the top was capped with a stopper. The tube was shaken vigorously to dissolve fat from the solid chocolate into the solvent. Caffeine and theobromine are insoluble in this solvent. The mixture of liquid and fine particles was then spun in a centrifuge to pack the chocolate at the bottom of the tube. The clear liquid, containing dissolved fat, could now be **decanted** (poured off) and discarded. Extraction with fresh portions of solvent was repeated twice more to ensure complete removal of fat from the chocolate. Residual solvent in the chocolate was finally removed by heating the centrifuge tube in a beaker of boiling water. The mass of chocolate residue could be calculated by weighing the centrifuge tube plus its content of defatted chocolate residue and subtracting the known mass of the empty tube.

Substances being measured—caffeine and theobromine in this case—are called **analytes.** The next step in the sample preparation procedure was to make a **quantitative transfer** (a complete transfer) of the fat-free chocolate residue to an Erlenmeyer flask and to dissolve the analytes in water for the chemical analysis. If any residue were not transferred from the tube to the flask, then the final analysis would be in error because not all of the analyte would be present. To perform the quantitative transfer, Denby and Scott added a few milliliters of pure water to the centrifuge tube and used stirring and heating to dissolve or suspend as much of the chocolate as possible. Then they poured the **slurry** (a suspension of solid in a liquid) into a 50-mL flask. They repeated the procedure several times with fresh portions of water to ensure that every bit of chocolate was transferred from the centrifuge tube to the flask.

To complete the dissolution of analytes, Denby and Scott added water to bring the volume up to about 30 mL. They heated the flask in a boiling water bath to extract all the caffeine and theobromine from the chocolate into the water. To compute the quantity of analyte later, the total mass of solvent (water) must be accurately known. Denby and Scott knew the mass of chocolate residue in the centrifuge tube and they knew the mass of the empty Erlenmeyer flask. So they put the flask on a balance and added water drop by drop until there were exactly 33.3 g of water in the flask. Later, they would compare known solutions of pure analyte in water with the unknown solution containing 33.3 g of water.

A solution of anything in water is called an aqueous solution.

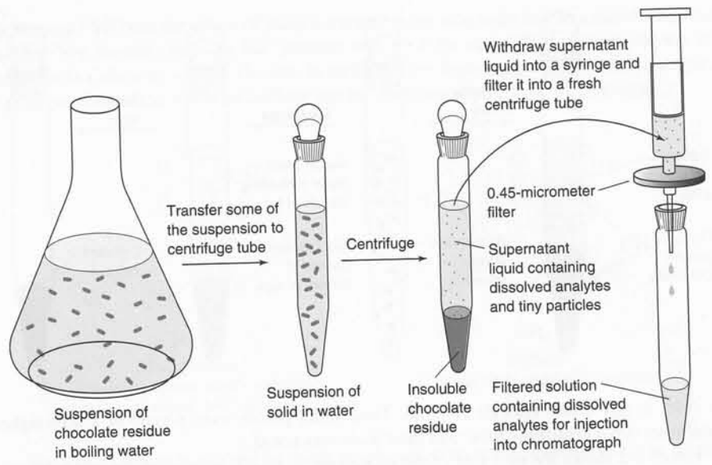
Before Denby and Scott could inject the unknown solution into a chromatograph for the chemical analysis, they had to clean up the unknown even further (Figure 0-3). The slurry of chocolate residue in water contained tiny solid particles that would surely clog their expensive chromatography column and ruin it. So they transferred a portion of the slurry to a centrifuge tube and centrifuged the mixture to pack as much of the solid as possible at the bottom of the tube. The cloudy, tan **supernatant liquid** (liquid above the packed solid) was then filtered in a further attempt to remove tiny particles of solid from the liquid.

It is critical to avoid injecting solids into a chromatography column, but the tan liquid still looked cloudy. So Denby and Scott took turns between classes to repeat the centrifugation and filtration five times. After each cycle in which the supernatant liquid was filtered and centrifuged, it became a little cleaner. But the liquid was never completely clear. Given enough time, more solid always seemed to precipitate from the filtered solution.

Real-life samples rarely cooperate with you!

The tedious procedure described so far is called **sample preparation**—transforming a sample into a state that is suitable for analysis. In this case, fat had to be removed from the

ure 0-3 Centrifugation and filtration are d to separate undesired solid residue from aqueous solution of analytes.



chocolate, analytes had to be extracted into water, and residual solid had to be separated from the water.

The Chemical Analysis (At Last!)

Denby and Scott finally decided that the solution of analytes was as clean as they could make it in the time available. The next step was to inject solution into a *chromatography* column, which would separate the analytes and measure the quantity of each. The column in Figure 0-4a is packed with tiny particles of silica (SiO_2) to which are attached long hydrocarbon molecules. Twenty microliters (20.0×10^{-6} liters) of the chocolate extract were injected into the column and washed through with a solvent made by mixing 79 mL of pure water, 20 mL of methanol, and 1 mL of acetic acid. Caffeine is more soluble than theobromine in the hydrocarbon on the silica surface. Therefore, caffeine "sticks" to the coated silica particles in the column more strongly than theobromine does. When both analytes are flushed through the column by solvent, theobromine reaches the outlet before caffeine (Figure 0-4b).

hromatography solvent is selected by a rstematic trial-and-error process described in hapter 25. The function of the acetic acid is react with negatively charged oxygen toms that lie on the silica surface and, when ot neutralized, tightly bind a small fraction of affeine and theobromine.

silica-O$^-$ $\xrightarrow{\text{acetic acid}}$ silica-OH

Binds analytes very tightly — Does not bind analytes strongly

Figure 0-4 Principle of liquid chromatography. (*a*) Chromatography apparatus with an ultraviolet absorbance monitor to detect analytes at the column outlet. (*b*) Separation of caffeine and theobromine by chromatography. Caffeine is more soluble than theobromine in the hydrocarbon layer on the particles in the column. Therefore, caffeine is retained more strongly and moves through the column more slowly than theobromine.

Analytes are detected at the outlet by their ability to absorb ultraviolet radiation from the lamp in Figure 0-4a. The graph of detector response versus time in Figure 0-5 is called a *chromatogram.* Theobromine and caffeine are the major peaks in the chromatogram. Small peaks arise from other substances extracted from the chocolate.

The chromatogram alone does not tell us what compounds are present. One way to identify individual peaks is to measure spectral characteristics of each one as it emerges from the column. Another way is to add an authentic sample of either caffeine or theobromine to the unknown and see whether one of the peaks grows in magnitude.

Identifying *what* is in an unknown is called **qualitative analysis.** Identifying *how much* is present is called **quantitative analysis.** The vast majority of this book deals with quantitative analysis.

In Figure 0-5, the *area* under each peak is proportional to the quantity of compound passing through the detector. The best way to measure area is with a computer that receives output from the chromatography detector. Denby and Scott did not have a computer linked to their chromatograph, so they measured the *height* of each peak instead.

Calibration Curves

In general, analytes with equal concentrations give different detector responses. Therefore, the response must be measured for known concentrations of each analyte. A graph of detector response as a function of analyte concentration is called a **calibration curve** or a *standard curve.* To construct such a curve, **standard solutions** containing known concentrations of pure theobromine or caffeine were prepared and injected into the column, and the resulting peak heights were measured. Figure 0-6 is a chromatogram of one of the standard solutions, and Figure 0-7 shows calibration curves made by injecting solutions containing 10.0, 25.0, 50.0, or 100.0 micrograms of each analyte per gram of solution.

Straight lines drawn through the calibration points could then be used to find the concentrations of theobromine and caffeine in an unknown. From the equation of the theobromine line in Figure 0-7, we can say that if the observed peak height of theobromine from an unknown solution is 15.0 cm, then the concentration is 76.9 micrograms per gram of solution.

Interpreting the Results

Knowing how much analyte is in the aqueous extract of the chocolate, Denby and Scott could calculate how much theobromine and caffeine were in the original chocolate. Results

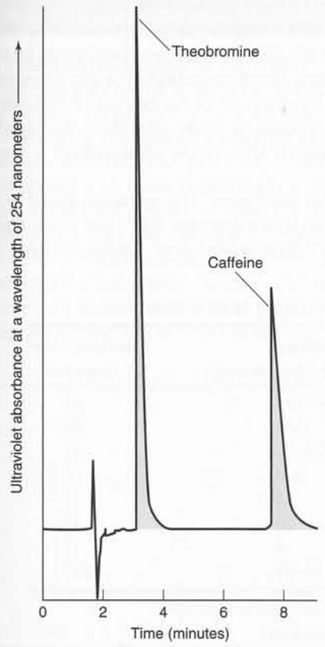


Figure 0-6 Chromatogram of 20.0 microliters of a standard solution containing 50.0 micrograms of theobromine and 50.0 micrograms of caffeine per gram of solution.

Only substances that absorb ultraviolet radiation at a wavelength of 254 nanometers are observed in Figure 0-5. By far, the major components in the aqueous extract are sugars, but they are not detected in this experiment.

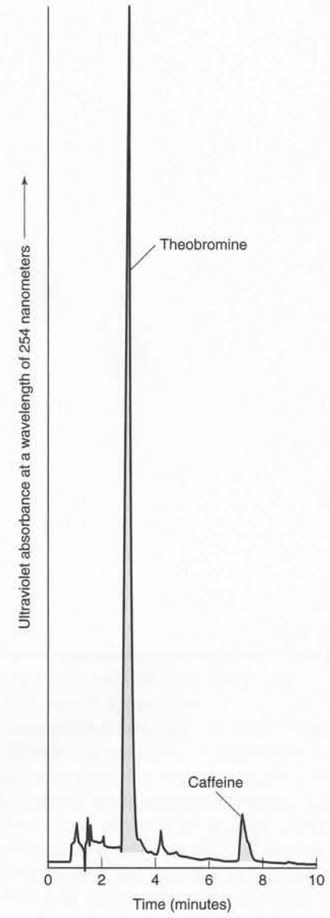
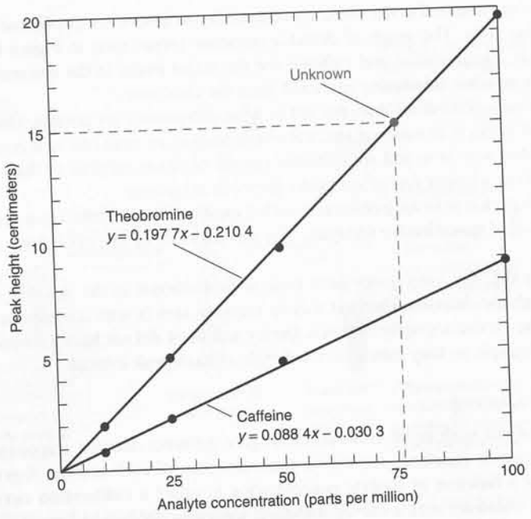


Figure 0-5 Chromatogram of 20.0 microliters of dark chocolate extract. A 4.6-mm-diameter × 150-mm-long column, packed with 5-micrometer particles of Hypersil ODS, was eluted (washed) with water:methanol:acetic acid (79:20:1 by volume) at a rate of 1.0 mL per minute.

gure 0-7 Calibration curves, showing served peak heights for known ncentrations of pure compounds. One part r million is one microgram of analyte per am of solution. Equations of the straight lines awn through the experimental data points ere determined by the *method of least uares*, described in Chapter 4.



for dark and white chocolates are shown in Table 0-1. The quantities found in white chocolate are only about 2% as great as the quantities in dark chocolate.

Table 0-1 Analyses of dark and white chocolate

	Grams of analyte per 100 grams of chocolate	
Analyte	**Dark chocolate**	**White chocolate**
Theobromine	0.392 ± 0.002	0.010 ± 0.007
Caffeine	0.050 ± 0.003	0.000 9 ± 0.001 4

Uncertainties are the standard deviation of three replicate injections of each extract.

The table also reports the *standard deviation* of three replicate measurements for each sample. Standard deviation, discussed in Chapter 4, is a measure of the reproducibility of the results. If three samples were to give identical results, the standard deviation would be 0. If results are not very reproducible, then the standard deviation is large. For theobromine in dark chocolate, the standard deviation (0.002) is less than 1% of the average (0.392), so we say the measurement is reproducible. For theobromine in white chocolate, the standard deviation (0.007) is nearly as great as the average (0.010), so the measurement is poorly reproducible.

The purpose of an analysis is to reach some conclusion. The questions posed at the beginning of this chapter were "How much caffeine is in a chocolate bar?" and "How does it compare with the quantity in coffee or soft drinks?" After all this work, Denby and Scott discovered how much caffeine is in the *one* particular chocolate bar that they analyzed. It would take a great deal more work to sample many chocolate bars of the same type and many different types of chocolate to gain a more universal view. Table 0-2 compares results from analyses of different sources of caffeine. A can of soft drink or a cup of tea contains less than one-half of the caffeine in a small cup of coffee. Chocolate contains even less caffeine, but a hungry backpacker eating enough baking chocolate can get a pretty good jolt!

Table 0-2 Caffeine content of beverages and foods

Source	Caffeine (milligrams per serving)	Serving size[a] (ounces)
Regular coffee	106–164	5
Decaffeinated coffee	2–5	5
Tea	21–50	5
Cocoa beverage	2–8	6
Baking chocolate	35	1
Sweet chocolate	20	1
Milk chocolate	6	1
Caffeinated soft drinks	36–57	12

a. 1 ounce = 28.35 grams.

SOURCE: Tea Association (http://www.chinamist.com/caffeine.htm).

0-2 General Steps in a Chemical Analysis

The analytical process often begins with a question that is not phrased in terms of a chemical analysis. The question could be "Is this water safe to drink?" or "Does emission testing of automobiles reduce air pollution?" A scientist translates such questions into the need for particular measurements. An analytical chemist then chooses or invents a procedure to carry out those measurements.

When the analysis is complete, the analyst must translate the results into terms that can be understood by others—preferably by the general public. A most important feature of any result is its limitations. What is the statistical uncertainty in reported results? If you took samples in a different manner, would you obtain the same results? Is a tiny amount (a *trace*) of analyte found in a sample really there or is it contamination? Only after we understand the results and their limitations can we draw conclusions.

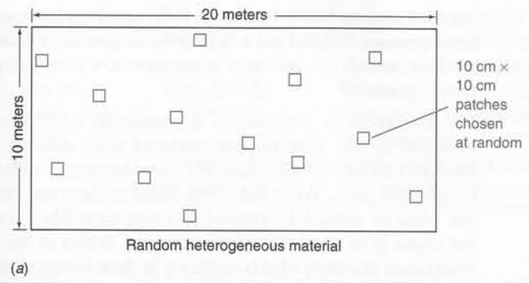
We can now summarize general steps in the analytical process:

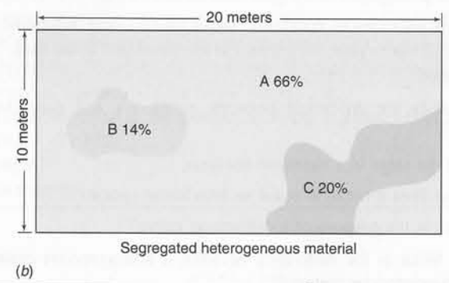
Formulating the question	Translate general questions into specific questions to be answered through chemical measurements.
Selecting analytical procedures	Search the chemical literature to find appropriate procedures or, if necessary, devise new procedures to make the required measurements.
Sampling	*Sampling* is the process of selecting representative material to analyze. Box 0-1 provides some ideas on how to do so. If you begin with a poorly chosen sample or if the sample changes between the time it is collected and the time it is analyzed, the results are meaningless. "Garbage in, garbage out!"

Box 0-1 Constructing a Representative Sample

In a **random heterogeneous material,** differences in composition occur randomly and on a fine scale. When you collect a portion of the material for analysis, you obtain some of each of the different compositions. To construct a representative sample from a heterogeneous material, you can first visually divide the material into segments. A **random sample** is collected by taking portions from the desired number of segments chosen at random. If you want to measure the magnesium content of the grass in the 10-meter × 20-meter field in panel (*a*), you could divide the field into 20 000 small patches that are 10 centimeters on a side. After assigning a number to each small patch, you could use a computer program to pick 100 numbers at random from 1 to 20 000. Then harvest and combine the grass from each of these 100 patches to construct a representative bulk sample for analysis.

For a **segregated heterogeneous material** (in which large regions have obviously different compositions), a representative **composite sample** must be constructed. For example, the field in panel (*b*) has three different types of grass segregated into regions A, B, and C. You could draw a map of the field on graph paper and measure the area in each region. In this case, 66% of the area lies in region A, 14% lies in region B, and 20% lies in region C. To construct a representative bulk sample from this segregated material, take 66 of the small patches from region A, 14 from region B, and 20 from region C. You could do so by drawing random numbers from 1 to 20 000 to select patches until you have the desired number from each region.





hemists use the term **species** to refer to any hemical of interest. Species is both singular nd plural. **Interference** occurs when a pecies other than analyte increases or ecreases the response of the analytical ethod and makes it appear that there is nore or less analyte than is actually present. **Masking** is the transformation of an interfering pecies into a form that is not detected. For xample, Ca^{2+} in lake water can be measured vith a reagent called EDTA. Al^{3+} interferes with his analysis, because it also reacts with EDTA. Al^{3+} can be masked by treating the sample vith excess F^- to form AlF_6^{3-}, which does not eact with EDTA.

Sample preparation — *Sample preparation* is the process of converting a representative sample into a form suitable for chemical analysis, which usually means dissolving the sample. Samples with a low concentration of analyte may need to be concentrated prior to analysis. It may be necessary to remove or *mask* species that interfere with the chemical analysis. For a chocolate bar, sample preparation consisted of removing fat and dissolving the desired analytes. The reason for removing fat was that it would interfere with chromatography.

Analysis — Measure the concentration of analyte in several identical **aliquots** (portions). The purpose of *replicate measurements* (repeated measurements) is to assess the variability (uncertainty) in the analysis and to guard against a gross error in the analysis of a single aliquot. *The uncertainty of a measurement is as important as the measurement itself,* because it tells us how reliable the measurement is. If necessary, use different analytical methods on similar samples to make sure that all methods give the same result and that the choice of analytical method is not biasing the result. You may also wish to construct and analyze several different bulk samples to see what variations arise from your sampling procedure.

Reporting and interpretation — Deliver a clearly written, complete report of your results, highlighting any limitations that you attach to them. Your report might be written to be read only by a specialist (such as your instructor) or it might be written for a general audience (perhaps your mother). Be sure the report is appropriate for its intended audience.

Drawing conclusions — Once a report is written, the analyst might not be involved in what is done with the information, such as modifying the raw material supply for a factory or creating new laws to regulate food additives. The more clearly a report is written, the less likely it is to be misinterpreted by those who use it.

Most of this book deals with measuring chemical concentrations in homogeneous aliquots of an unknown. The analysis is meaningless unless you have collected the sample properly, you have taken measures to ensure the reliability of the analytical method, and you communicate your results clearly and completely. The chemical analysis is only the middle portion of a process that begins with a question and ends with a conclusion.

Terms to Understand

Terms are introduced in **bold** type in the chapter and are also defined in the Glossary.

aliquot
analyte
aqueous
calibration curve
composite sample
decant
heterogeneous
homogeneous
interference
masking
qualitative analysis
quantitative analysis
quantitative transfer
random heterogeneous material
random sample
sample preparation
sampling
segregated heterogeneous material
slurry
species
standard solution
supernatant liquid

Problems

Complete solutions to Problems can be found in the *Solutions Manual*. Short answers to numerical problems are at the back of the book.

0-1. What is the difference between *qualitative* and *quantitative* analysis?

0-2. List the steps in a chemical analysis.

0-3. What does it mean to *mask* an interfering species?

0-4. What is the purpose of a calibration curve?

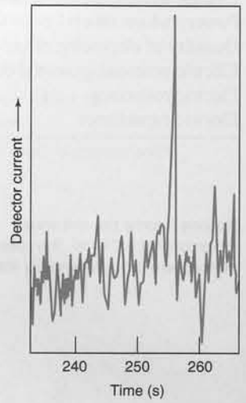
0-5. (a) What is the difference between a homogeneous material and a heterogeneous material? (b) After reading Box 0-1, state the difference between a segregated heterogeneous material and a random heterogeneous material. (c) How would you construct a representative sample from each type of material?

0-6. The iodide (I^-) content of a commercial mineral water was measured by two methods that produced wildy different results.[7] Method A found 0.23 milligrams of I^- per liter (mg/L) and method B found 0.009 mg/L. When Mn^{2+} was added to the water, the I^- content found by method A increased each time more Mn^{2+} was added, but results from method B were unchanged. Which of the *Terms to Understand* describes what is occurring in these measurements?

1 Measurements

ULTRASENSITIVE MEASUREMENT OF ATOMS IN A VAPOR

One of the ways we will learn to express quantities in Chapter 1 is by using prefixes such as *mega* for million (10^6), *micro* for one-millionth (10^{-6}), and atto for 10^{-18}. The illustration shows a signal due to light absorption by just *60 atoms* of rubidium in the cross-sectional area of a laser beam. There are 6.02×10^{23} atoms in a mole, so 60 atoms amount to 1.0×10^{-22} moles. With prefixes from Table 1-3, we will express this number as 100 *yoctomoles* (ymol) or 0.1 *zeptomole* (zmol). The prefix *yocto* stands for 10^{-24} and *zepto* stands for 10^{-21}. As chemists learn to measure fewer and fewer atoms or molecules, these strange-sounding prefixes become more and more common in the chemical literature.



Atomic absorption signal from 60 gaseous rubidium atoms observed by laser wave mixing. A 10-microliter (10×10^{-6} L) sample containing 1 attogram (1×10^{-18} g) of Rb^+ was injected into a graphite furnace to create the atomic vapor. We will study atomic absorption spectroscopy in Chapter 21. *[F. K. Mickadeit, S. Berniolles, H. R. Kemp, and W. G. Tong, Anal. Chem.* ***2004,*** *76, 1788.]*

Primed by an overview of the analytical process in Chapter 0, we are ready to discuss subjects required to get started in the lab. Topics include units of measurement, chemical concentrations, preparation of solutions, and the stoichiometry of chemical reactions.

1-1 SI Units

SI units of measurement, used by scientists around the world, derive their name from the French *Système International d'Unités*. *Fundamental units* (base units) from which all others are derived are defined in Table 1-1. Standards of length, mass, and time are the *meter* (m), *kilogram* (kg), and *second* (s), respectively. Temperature is measured in *kelvins* (K), amount of substance in *moles* (mol), and electric current in *amperes* (A).

For readability, we insert a space after every third digit on either side of the decimal point. Commas are not used because in some parts of the world a comma has the same meaning as a decimal point. Two examples:

speed of light: 299 792 458 m/s
Avogadro's number: 6.022 141 5 × 10^{23} mol^{-1}

Table 1-1 Fundamental SI units

Quantity	Unit (symbol)	Definition
Length	meter (m)	One meter is the distance light travels in a vacuum during $\frac{1}{299\,792\,458}$ of a second.
Mass	kilogram (kg)	One kilogram is the mass of the prototype kilogram kept at Sèvres, France.
Time	second (s)	One second is the duration of 9 192 631 770 periods of the radiation corresponding to a certain atomic transition of ^{133}Cs.
Electric current	ampere (A)	One ampere of current produces a force of 2×10^{-7} newtons per meter of length when maintained in two straight, parallel conductors of infinite length and negligible cross section, separated by 1 meter in a vacuum.
Temperature	kelvin (K)	Temperature is defined such that the triple point of water (at which solid, liquid, and gaseous water are in equilibrium) is 273.16 K, and the temperature of absolute zero is 0 K.
Luminous intensity	candela (cd)	Candela is a measure of luminous intensity visible to the human eye.
Amount of substance	mole (mol)	One mole is the number of particles equal to the number of atoms in exactly 0.012 kg of ^{12}C (approximately 6.022 141 5 × 10^{23}).
Plane angle	radian (rad)	There are 2π radians in a circle.
Solid angle	steradian (sr)	There are 4π steradians in a sphere.

ble 1-2 SI-derived units with special names

uantity	Unit	Symbol	Expression in terms of other units	Expression in terms of SI base units
equency	hertz	Hz		l/s
rce	newton	N		$m \cdot kg/s^2$
essure	pascal	Pa	N/m^2	$kg/(m \cdot s^2)$
ergy, work, quantity of heat	joule	J	$N \cdot m$	$m^2 \cdot kg/s^2$
wer, radiant flux	watt	W	J/s	$m^2 \cdot kg/s^3$
uantity of electricity, electric charge	coulomb	C		$s \cdot A$
lectric potential, potential difference, electromotive force	volt	V	W/A	$m^2 \cdot kg/(s^3 \cdot A)$
lectric resistance	ohm	Ω	V/A	$m^2 \cdot kg/(s^3 \cdot A^2)$
lectric capacitance	farad	F	C/V	$s^4 \cdot A^2/(m^2 \cdot kg)$

ressure is force per unit area:
pascal (Pa) = 1 N/m². The pressure of the
tmosphere is approximately 100 000 Pa.

Table 1-2 lists some quantities that are defined in terms of the fundamental quantities. For example, force is measured in *newtons* (N), pressure is measured in *pascals* (Pa), and energy is measured in *joules* (J), each of which can be expressed in terms of the more fundamental units of length, time, and mass.

Using Prefixes as Multipliers

Rather than using exponential notation, we often use prefixes from Table 1-3 to express large or small quantities. As an example, consider the pressure of ozone (O_3) in the upper atmosphere (Figure 1-1). Ozone is important because it absorbs ultraviolet radiation from the sun that damages many organisms and causes skin cancer. Each spring, a great deal of ozone disappears from the Antarctic stratosphere, thereby creating what is called an ozone "hole." The opening of Chapter 18 discusses the chemistry behind this process.

At an altitude of 1.7×10^4 meters above the earth's surface, the pressure of ozone over Antarctica reaches a peak of 0.019 Pa. Let's express these numbers with prefixes from Table 1-3. We customarily use prefixes for every third power of ten (10^{-9}, 10^{-6}, 10^{-3}, 10^3, 10^6, 10^9, and so on). The number 1.7×10^4 m is more than 10^3 m and less than 10^6 m, so we use a multiple of 10^3 m (= kilometers, km):

$$1.7 \times 10^4 \text{ m} \times \frac{1 \text{ km}}{10^3 \text{ m}} = 1.7 \times 10^1 \text{ km} = 17 \text{ km}$$

The number 0.019 Pa is more than 10^{-3} Pa and less than 10^0 Pa, so we use a multiple of 10^{-3} Pa (= millipascals, mPa):

$$0.019 \text{ Pa} \times \frac{1 \text{ mPa}}{10^{-3} \text{ Pa}} = 1.9 \times 10^1 \text{ mPa} = 19 \text{ mPa}$$

Figure 1-1 is labeled with km on the *y*-axis and mPa on the *x*-axis. The *y*-axis of any graph is called the **ordinate** and the *x*-axis is called the **abscissa.**

It is a fabulous idea to write units beside each number in a calculation and to cancel identical units in the numerator and denominator. This practice ensures that you know the

Of course you recall that $10^0 = 1$.

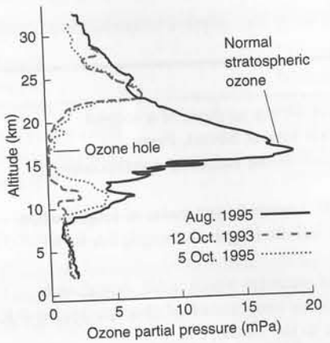


Figure 1-1 An ozone "hole" forms each year in the stratosphere over the South Pole at the beginning of spring in October. The graph compares ozone pressure in August, when there is no hole, with the pressure in October, when the hole is deepest. Less severe ozone loss is observed at the North Pole. *[Data from National Oceanic and Atmospheric Administration.]*

Table 1-3 Prefixes

Prefix	Symbol	Factor	Prefix	Symbol	Factor
yotta	Y	10^{24}	deci	d	10^{-1}
zetta	Z	10^{21}	centi	c	10^{-2}
exa	E	10^{18}	milli	m	10^{-3}
peta	P	10^{15}	micro	μ	10^{-6}
tera	T	10^{12}	nano	n	10^{-9}
giga	G	10^9	pico	p	10^{-12}
mega	M	10^6	femto	f	10^{-15}
kilo	k	10^3	atto	a	10^{-18}
hecto	h	10^2	zepto	z	10^{-21}
deca	da	10^1	yocto	y	10^{-24}

units for your answer. If you intend to calculate pressure and your answer comes out with units other than pascals (or some other unit of pressure), then you know you have made a mistake.

Converting Between Units

Although SI is the internationally accepted system of measurement in science, other units are encountered. Useful conversion factors are found in Table 1-4. For example, common non-SI units for energy are the *calorie* (cal) and the *Calorie* (with a capital C, which stands for 1 000 calories, or 1 kcal). Table 1-4 states that 1 cal is exactly 4.184 J (joules).

Your *basal metabolism* requires approximately 46 Calories per hour (h) per 100 pounds (lb) of body mass to carry out basic functions required for life, apart from doing any kind of exercise. A person walking at 2 miles per hour on a level path requires approximately 45 Calories per hour per 100 pounds of body mass beyond basal metabolism. The same person swimming at 2 miles per hour consumes 360 Calories per hour per 100 pounds beyond basal metabolism.

One *calorie* is the energy required to heat 1 gram of water from 14.5° to 15.5°C.
One *joule* is the energy expended when a force of 1 newton acts over a distance of 1 meter. This much energy can raise 102 g (about $\frac{1}{4}$ pound) by 1 meter.

1 cal = 4.184 J

1 pound (mass) ≈ 0.453 6 kg

1 mile ≈ 1.609 km

The symbol ≈ is read "is approximately equal to."

Example Unit Conversions

Express the rate of energy used by a person walking 2 miles per hour (46 + 45 = 91 Calories per hour per 100 pounds of body mass) in kilojoules per hour per kilogram of body mass.

Solution We will convert each non-SI unit separately. First, note that 91 Calories equals 91 kcal. Table 1-4 states that 1 cal = 4.184 J; so 1 kcal = 4.184 kJ, and

$$91 \cancel{\text{kcal}} \times 4.184 \frac{\text{kJ}}{\cancel{\text{kcal}}} = 3.8 \times 10^2 \text{ kJ}$$

Table 1-4 also says that 1 lb is 0.453 6 kg; so 100 lb = 45.36 kg. The rate of energy consumption is therefore

$$\frac{91 \text{ kcal/h}}{100 \text{ lb}} = \frac{3.8 \times 10^2 \text{ kJ/h}}{45.36 \text{ kg}} = 8.4 \frac{\text{kJ/h}}{\text{kg}}$$

We could have written this as one long calculation:

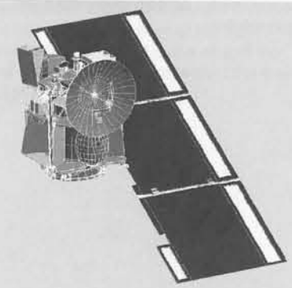
$$\text{Rate} = \frac{91 \cancel{\text{kcal}}/\text{h}}{100 \cancel{\text{lb}}} \times 4.184 \frac{\text{kJ}}{\cancel{\text{kcal}}} \times \frac{1 \cancel{\text{lb}}}{0.453\,6 \text{ kg}} = 8.4 \frac{\text{kJ/h}}{\text{kg}}$$

Significant figures are discussed in Chapter 3. For multiplication and division, the number with the fewest digits determines how many digits should be in the answer. The number 91 kcal at the beginning of this problem limits the answer to 2 digits.

Table 1-4 Conversion factors

Quantity	Unit	Symbol	SI equivalent[a]
Volume	liter	L	$*10^{-3}$ m³
	milliliter	mL	$*10^{-6}$ m³
Length	angstrom	Å	$*10^{-10}$ m
	inch	in.	*0.025 4 m
Mass	pound	lb	*0.453 592 37 kg
	metric ton		*1 000 kg
Force	dyne	dyn	$*10^{-5}$ N
Pressure	bar	bar	$*10^5$ Pa
	atmosphere	atm	*101 325 Pa
	torr (= 1 mm Hg)	Torr	133.322 Pa
	pound/in.²	psi	6 894.76 Pa
Energy	erg	erg	$*10^{-7}$ J
	electron volt	eV	$1.602\,176\,53 \times 10^{-19}$ J
	calorie, thermochemical	cal	*4.184 J
	Calorie (with a capital C)	Cal	*1 000 cal = 4.184 kJ
	British thermal unit	Btu	1 055.06 J
Power	horsepower		745.700 W
Temperature	centigrade (= Celsius)	°C	*K − 273.15
	Fahrenheit	°F	*1.8(K − 273.15) + 32

a. An asterisk (*) indicates that the conversion is exact (by definition).



Write the units: In 1999, the $125 million *Mars Climate Orbiter* spacecraft was lost when it entered the Martian atmosphere 100 km lower than planned. *The navigation error would have been avoided if people had labeled their units of measurement.* Engineers who built the spacecraft calculated thrust in the English unit, pounds of force. Jet Propulsion Laboratory engineers thought they were receiving the information in the metric unit, newtons. Nobody caught the error.

omogeneous means that the mixture has the me composition everywhere. When sugar ssolves in water, the mixture is homogeneous. mixture that is not the same everywhere uch as orange juice, which has suspended olids) is *heterogeneous*.

vogadro's number = number of atoms in 12 g of ^{12}C

Molarity (M) = $\frac{\text{moles of solute}}{\text{liters of solution}}$

Atomic masses are shown in the periodic able inside the cover of this book. Physical constants such as Avogadro's number are also listed inside the cover.

1-2 Chemical Concentrations

A *solution* is a *homogeneous* mixture of two or more substances. A minor species in a solution is called **solute** and the major species is the **solvent.** In this book, most discussions concern *aqueous solutions,* in which the solvent is water. **Concentration** states how much solute is contained in a given volume or mass of solution or solvent.

Molarity and Molality

A **mole** (mol) is *Avogadro's number* of particles (atoms, molecules, ions, or anything else). **Molarity** (M) is the number of moles of a substance per liter of solution. A **liter** (L) is the volume of a cube that is 10 cm on each edge. Because 10 cm = 0.1 m, 1 L = $(0.1\ \text{m})^3$ = $10^{-3}\ \text{m}^3$. Chemical concentrations, denoted with square brackets, are usually expressed in moles per liter (M). Thus "$[H^+]$" means "the concentration of H^+."

The **atomic mass** of an element is the number of grams containing Avogadro's number of atoms.[1] The **molecular mass** of a compound is the sum of atomic masses of the atoms in the molecule. It is the number of grams containing Avogadro's number of molecules.

Example Molarity of Salts in the Sea

(a) Typical seawater contains 2.7 g of salt (sodium chloride, NaCl) per 100 mL (= 100 × 10^{-3} L). What is the molarity of NaCl in the ocean? **(b)** $MgCl_2$ has a concentration of 0.054 M in the ocean. How many grams of $MgCl_2$ are present in 25 mL of seawater?

Solution **(a)** The molecular mass of NaCl is 22.99 g/mol (Na) + 35.45 g/mol (Cl) = 58.44 g/mol. The moles of salt in 2.7 g are (2.7 g)/(58.44 g/mol) = 0.046 mol, so the molarity is

$$\text{Molarity of NaCl} = \frac{\text{mol NaCl}}{\text{L of seawater}} = \frac{0.046\ \text{mol}}{100 \times 10^{-3}\ \text{L}} = 0.46\,\text{M}$$

(b) The molecular mass of $MgCl_2$ is 24.30 g/mol (Mg) + 2 × 35.45 g/mol (Cl) = 95.20 g/mol. The number of grams in 25 mL is

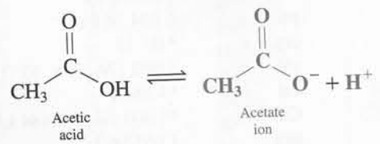
$$\text{Grams of } MgCl_2 = \left(0.054\ \frac{\cancel{\text{mol}}}{\cancel{\text{L}}}\right)\left(95.20\ \frac{\text{g}}{\cancel{\text{mol}}}\right)(25 \times 10^{-3}\ \cancel{\text{L}}) = 0.13\ \text{g}$$

Strong electrolyte: mostly dissociated into ions in solution
Weak electrolyte: partially dissociated into ions in solution

An **electrolyte** is a substance that dissociates into ions in solution. In general, electrolytes are more dissociated in water than in other solvents. We refer to a compound that is mostly dissociated into ions as a *strong electrolyte.* One that is partially dissociated is called a *weak electrolyte.*

Magnesium chloride is a strong electrolyte. In 0.44 M $MgCl_2$ solution, 70% of the magnesium is free Mg^{2+} and 30% is $MgCl^+$.[2] The concentration of $MgCl_2$ molecules is close to 0. Sometimes the molarity of a strong electrolyte is called the **formal concentration** (F), to emphasize that the substance is really converted into other species in solution. When we say that the "concentration" of $MgCl_2$ is 0.054 M in seawater, we are really referring to its formal concentration (0.054 F). The "molecular mass" of a strong electrolyte is called the **formula mass** (FM), because it is the sum of atomic masses of atoms in the formula, even though there are very few molecules with that formula. *We are going to use the abbreviation FM for both formula mass and molecular mass.*

For a *weak electrolyte* such as acetic acid, CH_3CO_2H, some of the molecules dissociate into ions in solution:



Formal concentration	Percent dissociated
0.10 F	1.3%
0.010 F	4.1%
0.001 0 F	12%

Confusing abbreviations:
mol = moles
M = molarity = $\frac{\text{mol solute}}{\text{L solution}}$
m = molality = $\frac{\text{mol solute}}{\text{kg solvent}}$

Molality (*m*) is concentration expressed as moles of substance per kilogram of solvent (not total solution). Molality is independent of temperature. Molarity changes with temperature because the volume of a solution usually increases when it is heated.

Percent Composition

The percentage of a component in a mixture or solution is usually expressed as a **weight percent** (wt%):

$$\text{Weight percent} = \frac{\text{mass of solute}}{\text{mass of total solution or mixture}} \times 100 \qquad (1\text{-}1)$$

A common form of ethanol (CH_3CH_2OH) is 95 wt%; this expression means 95 g of ethanol per 100 g of total solution. The remainder is water. **Volume percent** (vol%) is defined as

$$\text{Volume percent} = \frac{\text{volume of solute}}{\text{volume of total solution}} \times 100 \qquad (1\text{-}2)$$

Although units of mass or volume should always be expressed to avoid ambiguity, mass is usually implied when units are absent.

Example Converting Weight Percent into Molarity and Molality

Find the molarity and molality of 37.0 wt% HCl. The **density** of a substance is the mass per unit volume. The table inside the back cover of this book tells us that the density of the reagent is 1.19 g/mL.

Density = $\frac{\text{mass}}{\text{volume}} = \frac{\text{g}}{\text{mL}}$

A closely related dimensionless quantity is

Specific gravity = $\frac{\text{density of a substance}}{\text{density of water at 4°C}}$

Because the density of water at 4°C is very close to 1 g/mL, specific gravity is nearly the same as density.

Solution For *molarity,* we need to find the moles of HCl per liter of solution. The mass of a liter of solution is (1.19 g/$\cancel{\text{mL}}$)(1 000 $\cancel{\text{mL}}$) = 1.19×10^3 g. The mass of HCl in a liter is

$$\text{Mass of HCl per liter} = \left(1.19 \times 10^3\ \frac{\cancel{\text{g solution}}}{\text{L}}\right)\underbrace{\left(0.370\ \frac{\text{g HCl}}{\cancel{\text{g solution}}}\right)}_{\substack{\text{This is what}\\ \text{37.0 wt\% means}}} = 4.40 \times 10^2\ \frac{\text{g HCl}}{\text{L}}$$

The molecular mass of HCl is 36.46 g/mol, so the molarity is

$$\text{Molarity} = \frac{\text{mol HCl}}{\text{L solution}} = \frac{4.40 \times 10^2\ \cancel{\text{g HCl}}/\text{L}}{36.46\ \cancel{\text{g HCl}}/\text{mol}} = 12.1\ \frac{\text{mol}}{\text{L}} = 12.1\ \text{M}$$

For *molality,* we need to find the moles of HCl per kilogram of solvent (which is H_2O). The solution is 37.0 wt% HCl, so we know that 100.0 g of solution contains 37.0 g of HCl and 100.0 − 37.0 = 63.0 g of H_2O (= 0.063 0 kg). But 37.0 g of HCl contains 37.0 g/(36.46 g/mol) = 1.01 mol. The molality is therefore

$$\text{Molality} = \frac{\text{mol HCl}}{\text{kg of solvent}} = \frac{1.01\ \text{mol HCl}}{0.063\ 0\ \text{kg}\ H_2O} = 16.1\ m$$

If you divide 1.01/0.063 0, you get 16.0. Dan got 16.1 because he kept all the digits in his calculator and did not round off until the end. The number 1.01 was really 1.014 8 and (1.014 8)/(0.063 0) = 16.1.

Figure 1-2 illustrates a weight percent measurement in the application of analytical chemistry to archaeology. Gold and silver are found together in nature. Dots in Figure 1-2 show the weight percent of gold in more than 1 300 silver coins minted over a 500-year period. Prior to A.D. 500, it was rare for the gold content to be below 0.3 wt%. By A.D. 600, people had developed techniques for removing more gold from the silver, so some coins had as little as 0.02 wt% gold. Colored squares in Figure 1-2 represent known, modern forgeries made from silver whose gold content is always less than the prevailing gold content in the years A.D. 200 to 500. Chemical analysis makes it easy to detect the forgeries.

Parts per Million and Parts per Billion

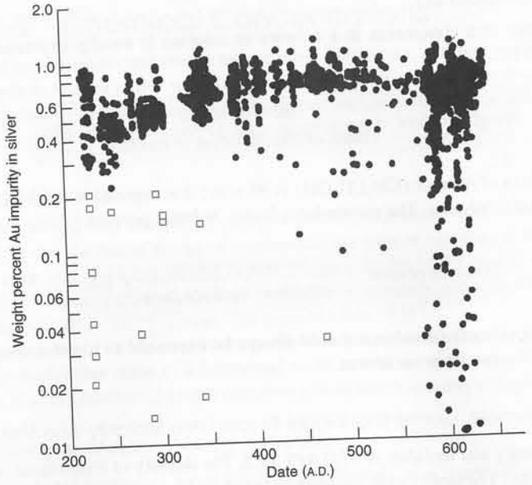
Sometimes composition is expressed as **parts per million** (ppm) or **parts per billion** (ppb), which mean grams of substance per million or billion grams of total solution or mixture. Because the density of a dilute aqueous solution is close to 1.00 g/mL, *we frequently equate 1 g of water with 1 mL of water,* although this equivalence is only approximate. Therefore, 1 ppm corresponds to 1 μg/mL (= 1 mg/L) and 1 ppb is 1 ng/mL (= 1 μg/L). For gases, ppm usually refers to volume rather than mass. Atmospheric CO_2 has a concentration near 380 ppm, which means 380 μL CO_2 per liter of air. It is best to label units to avoid confusion.

ppm = $\frac{\text{mass of substance}}{\text{mass of sample}} \times 10^6$

ppb = $\frac{\text{mass of substance}}{\text{mass of sample}} \times 10^9$

Question What does one part per thousand mean?

gure 1-2 Weight percent of gold impurity silver coins from Persia. Colored squares are own, modern forgeries. Note that the dinate scale is logarithmic. *[A. A. Gordus and P. Gordus, Archaeological Chemistry, Adv. Chem. o. 138, American Chemical Society, Washington, DC, 974, pp. 124–147.]*



Example Converting Parts per Billion into Molarity

Normal alkanes are hydrocarbons with the formula C_nH_{2n+2}. Plants selectively synthesize alkanes with an odd number of carbon atoms. The concentration of $C_{29}H_{60}$ in summer rainwater collected in Hannover, Germany, is 34 ppb. Find the molarity of $C_{29}H_{60}$ and express the answer with a prefix from Table 1-3.

Solution A concentration of 34 ppb means there are 34 ng of $C_{29}H_{60}$ per gram of rainwater, a value that we equate to 34 ng/mL. Multiplying nanograms and milliliters by 1 000 gives 34 μg of $C_{29}H_{60}$ per liter of rainwater. Because the molecular mass of $C_{29}H_{60}$ is 408.8 g/mol, the molarity is

$$\text{Molarity of } C_{29}H_{60} \text{ in rainwater} = \frac{34 \times 10^{-6}\ \text{g/L}}{408.8\ \text{g/mol}} = 8.3 \times 10^{-8}\ \text{M}$$

An appropriate prefix from Table 1-3 would be nano (n), which is a multiple of 10^{-9}:

$$8.3 \times 10^{-8}\ \text{M}\left(\frac{1\ \text{nM}}{10^{-9}\ \text{M}}\right) = 83\ \text{nM}$$

1-3 Preparing Solutions

To prepare a solution with a desired molarity from a pure solid or liquid, we weigh out the correct mass of reagent and dissolve it in the desired volume in a *volumetric flask* (Figure 1-3).

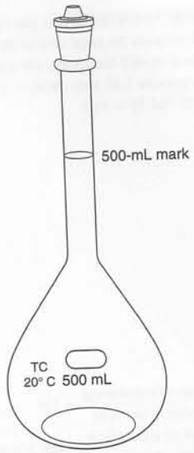


Figure 1-3 A *volumetric flask* contains a specified volume when the liquid level is adjusted to the middle of the mark in the thin neck of the flask. Use of this flask is described in Section 2-5.

Example Preparing a Solution with a Desired Molarity

Copper(II) sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$, has 5 moles of H_2O for each mole of $CuSO_4$ in the solid crystal. The formula mass of $CuSO_4 \cdot 5H_2O$ ($= CuSO_9H_{10}$) is 249.69 g/mol. (Copper(II) sulfate without water in the crystal has the formula $CuSO_4$ and is said to be **anhydrous.**) How many grams of $CuSO_4 \cdot 5H_2O$ should be dissolved in a volume of 500.0 mL to make 8.00 mM Cu^{2+}?

Solution An 8.00 mM solution contains 8.00×10^{-3} mol/L. We need

$$8.00 \times 10^{-3}\ \frac{\text{mol}}{\cancel{\text{L}}} \times 0.500\,0\ \cancel{\text{L}} = 4.00 \times 10^{-3}\ \text{mol } CuSO_4 \cdot 5H_2O$$

$$\text{The mass of reagent is } (4.00 \times 10^{-3}\ \cancel{\text{mol}}) \times \left(249.69\ \frac{\text{g}}{\cancel{\text{mol}}}\right) = 0.999\ \text{g}.$$

Using a volumetric flask: The procedure is to place 0.999 g of solid $CuSO_4 \cdot 5H_2O$ into a 500-mL volumetric flask, add about 400 mL of distilled water, and swirl to dissolve the reagent. Then dilute with distilled water up to the 500-mL mark and invert the flask several times to ensure complete mixing.

Dilution

Dilute solutions can be prepared from concentrated solutions. A volume of the concentrated solution is transferred to a fresh vessel and diluted to the desired final volume. The number of moles of reagent in V liters containing M moles per liter is the product $M \cdot V = \text{mol}/\cancel{\text{L}} \cdot \cancel{\text{L}}$, so we equate the number of moles in the concentrated (conc) and dilute (dil) solutions:

Dilution formula:

$$\underbrace{M_{conc} \cdot V_{conc}}_{\text{Moles taken from concentrated solution}} = \underbrace{M_{dil} \cdot V_{dil}}_{\text{Moles placed in dilute solution}} \qquad (1\text{-}3)$$

You may use any units for concentration and volume in this equation, as long as you use the same units on both sides. We frequently use mL for volume.

Example Preparing 0.100 M HCl

The molarity of "concentrated" HCl purchased for laboratory use is approximately 12.1 M. How many milliliters of this reagent should be diluted to 1.000 L to make 0.100 M HCl?

Solution The dilution formula handles this problem directly:

$$M_{conc} \cdot V_{conc} = M_{dil} \cdot V_{dil}$$

$$(12.1\ \text{M}) \cdot (x\ \text{mL}) = (0.100\ \text{M}) \cdot (1\,000\ \text{mL}) \Rightarrow x = 8.26\ \text{mL}$$

The symbol ⇒ is read "implies that."

To make 0.100 M HCl, we would dilute 8.26 mL of concentrated HCl up to 1.000 L. The concentration will not be exactly 0.100 M, because the reagent is not exactly 12.1 M. A table inside the cover of this book gives volumes of common reagents required to make 1.0 M solutions.

Example A More Complicated Dilution Calculation

A solution of ammonia in water is called "ammonium hydroxide" because of the equilibrium

$$\underset{\text{Ammonia}}{NH_3} + H_2O \rightleftharpoons \underset{\text{Ammonium}}{NH_4^+} + \underset{\text{Hydroxide}}{OH^-} \qquad (1\text{-}4)$$

In a chemical reaction, species on the left side are called **reactants** and species on the right are called **products**. NH_3 is a reactant and NH_4^+ is a product in Reaction 1-4.

The density of concentrated ammonium hydroxide, which contains 28.0 wt% NH_3, is 0.899 g/mL. What volume of this reagent should be diluted to 500.0 mL to make 0.250 M NH_3?

Solution To use Equation 1-3, we need to know the molarity of the concentrated reagent. The solution contains 0.899 g of solution per milliliter and there is 0.280 g of NH_3 per gram of solution (28.0 wt%), so we can write

$$\text{Molarity of } NH_3 = \frac{899\ \frac{\cancel{\text{g solution}}}{\text{L}} \times 0.280\ \frac{\cancel{\text{g NH}_3}}{\cancel{\text{g solution}}}}{17.03\ \frac{\cancel{\text{g NH}_3}}{\text{mol NH}_3}} = 14.8\ \text{M}$$

Now we find the volume of 14.8 M NH_3 required to prepare 500.0 mL of 0.250 M NH_3:

$$M_{conc} \cdot V_{conc} = M_{dil} \cdot V_{dil}$$

$$14.8\ \cancel{\text{M}} \times V_{conc} = 0.250\ \cancel{\text{M}} \times 500.0\ \text{mL} \Rightarrow V_{conc} = 8.45\ \text{mL}$$

The procedure is to place 8.45 mL of concentrated reagent in a 500-mL volumetric flask, add about 400 mL of water, and swirl to mix. Then dilute to exactly 500 mL with water and invert the flask many times to mix well.

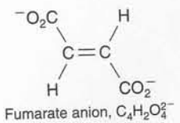
1-4 Stoichiometry Calculations

Stoichiometry is the calculation of quantities of substances involved in a chemical reaction. It is derived from the Greek *stoicheion* (simplest component) and *metiri* (to measure).

Let's apply concepts from preceding sections to a chemical analysis. Iron from a dietary supplement tablet can be measured by dissolving it and then converting the iron into solid Fe_2O_3. From the mass of Fe_2O_3, we can calculate the mass of iron in the original tablet. Chemical analysis based on weighing a final product is called *gravimetric analysis.*

Here are the steps in the procedure:

Step 1 Tablets containing iron(II) fumarate ($Fe^{2+}C_4H_2O_4^{2-}$) and inert binder are mixed with 150 mL of 0.100 M HCl to dissolve the Fe^{2+}. The solution is filtered to remove insoluble binder.



Fumarate anion, $C_4H_2O_4^{2-}$

The units of formula mass (FM) are g/mol.

Step 2 Iron(II) in the clear liquid is oxidized to iron(III) with excess hydrogen peroxide:

$$\underset{\substack{\text{Iron(II)}\\\text{(ferrous ion)}}}{2Fe^{2+}} + \underset{\substack{\text{Hydrogen peroxide}\\\text{FM 34.01}}}{H_2O_2} + 2H^+ \rightarrow \underset{\substack{\text{Iron(III)}\\\text{(ferric ion)}}}{2Fe^{3+}} + 2H_2O \qquad (1\text{-}5)$$

Step 3 Ammonium hydroxide is added to precipitate hydrous iron(III) oxide, which is a gel. The gel is filtered and heated in a furnace to convert it into pure solid Fe_2O_3.

$$\underset{\text{Hydroxide}}{Fe^{3+} + 3OH^-} + (x-1)H_2O \rightarrow \underset{\text{Hydrous iron(III) oxide}}{FeOOH \cdot xH_2O(s)} \xrightarrow{900^\circ C} \underset{\substack{\text{Iron(III) oxide}\\\text{FM 159.69}}}{Fe_2O_3(s)} \qquad (1\text{-}6)$$

We now work through some practical laboratory calculations for this analysis.

Example How Many Tablets Should We Analyze?

In a gravimetric analysis, we need enough product to weigh accurately. Each tablet provides ~15 mg of iron. How many tablets should we analyze to provide 0.25 g of Fe_2O_3 product?

Solution We can answer the question if we know how many grams of iron are in 0.25 g of Fe_2O_3. The formula mass of Fe_2O_3 is 159.69 g/mol, so 0.25 g is equal to

$$\text{mol } Fe_2O_3 = \frac{0.25\ \text{g}}{159.69\ \text{g/mol}} = 1.6 \times 10^{-3}\ \text{mol}$$

$$\text{mol} = \frac{\text{grams}}{\text{grams per mol}} = \frac{\text{grams}}{\text{formula mass}}$$

Each mol of Fe_2O_3 has 2 mol of Fe, so 0.25 g of Fe_2O_3 contains

$$1.6 \times 10^{-3}\ \cancel{\text{mol } Fe_2O_3} \times \frac{2\ \text{mol Fe}}{1\ \cancel{\text{mol } Fe_2O_3}} = 3.2 \times 10^{-3}\ \text{mol Fe}$$

The mass of Fe is

$$3.2 \times 10^{-3}\ \cancel{\text{mol Fe}} \times \frac{55.845\ \text{g Fe}}{\cancel{\text{mol Fe}}} = 0.18\ \text{g Fe}$$

The atomic mass of Fe, 55.845 g/mol, is in the periodic table inside the cover.

If each tablet contains 15 mg Fe, the number of tablets required is

$$\text{Number of tablets} = \frac{0.18\ \cancel{\text{g Fe}}}{0.015\ \cancel{\text{g Fe}}/\text{tablet}} = 12\ \text{tablets}$$

Example How Much H_2O_2 Is Required?

What mass of 3.0 wt% H_2O_2 solution is required to provide a 50% excess of reagent for Reaction 1-5 with 12 dietary iron tablets?

Solution Twelve tablets provide 12 $\cancel{\text{tablets}} \times (0.015\ \text{g}/\cancel{\text{tablet}}) = 0.18$ g of Fe^{2+}, or $(0.18\ \cancel{\text{g Fe}^{2+}})/(55.845\ \cancel{\text{g Fe}^{2+}}/\text{mol Fe}^{2+}) = 3.2 \times 10^{-3}$ mol Fe^{2+}. Reaction 1-5 requires 1 mol of H_2O_2 for every 2 mol of Fe^{2+}. Therefore 3.2×10^{-3} mol Fe^{2+} requires $(3.2 \times 10^{-3}\ \cancel{\text{mol Fe}^{2+}})(1\ \text{mol } H_2O_2/2\ \cancel{\text{mol Fe}^{2+}}) = 1.6 \times 10^{-3}$ mol H_2O_2. A 50% excess means that we want to use 1.50 times the stoichiometric quantity: $(1.50)(1.6 \times 10^{-3}\ \text{mol } H_2O_2) = 2.4 \times 10^{-3}$ mol H_2O_2. The formula mass of H_2O_2 is 34.01 g/mol, so the required mass of pure H_2O_2 is $(2.4 \times 10^{-3}\ \cancel{\text{mol}})(34.01\ \text{g}/\cancel{\text{mol}}) = 0.082$ g. But hydrogen peroxide is available as a 3.0 wt% solution, so the required mass of solution is

$$\text{Mass of } H_2O_2 \text{ solution} = \frac{0.082\ \cancel{\text{g } H_2O_2}}{0.030\ \cancel{\text{g } H_2O_2}/\text{g solution}} = 2.7\ \text{g solution}$$

$$\text{Moles} = \frac{\text{grams}}{\text{formula mass}} = \frac{\text{g}}{\text{g/mol}}$$

You should be able to use this relationship in your sleep.

The symbol ~ is read "approximately."

Example The Gravimetric Calculation

The final mass of Fe_2O_3 isolated at the end of the experiment was 0.277 g. What is the average mass of iron per dietary tablet?

Solution The moles of isolated Fe_2O_3 are (0.277 g)/(159.69 g/mol) = 1.73×10^{-3} mol. There are 2 mol Fe per formula unit, so the moles of Fe in the product are

$$(1.73 \times 10^{-3}\ \cancel{\text{mol } Fe_2O_3})\left(\frac{2\ \text{mol Fe}}{1\ \cancel{\text{mol } Fe_2O_3}}\right) = 3.47 \times 10^{-3}\ \text{mol Fe}$$

The mass of Fe is $(3.47 \times 10^{-3}\ \cancel{\text{mol Fe}})(55.845\ \text{g Fe}/\cancel{\text{mol Fe}}) = 0.194$ g Fe. Each of the 12 tablets therefore contains an average of (0.194 g Fe)/12 = 0.016 1 g = 16.1 mg.

Retain all the digits in your calculator during a series of calculations. The product 1.73×2 is not 3.47; but, with the extra digits in the calculator, the correct answer is 3.47 because 1.73 was really 1.734 6.

Terms to Understand

Terms are introduced in **bold** type in the chapter and are also defined in the Glossary.

abscissa	formal concentration	molecular mass	SI units
anhydrous	formula mass	ordinate	solute
atomic mass	liter	ppb (parts per billion)	solvent
concentration	molality	ppm (parts per million)	volume percent
density	molarity	product	weight percent
electrolyte	mole	reactant	

Summary

SI base units include the meter (m), kilogram (kg), second (s), ampere (A), kelvin (K), and mole (mol). Derived quantities such as force (newton, N), pressure (pascal, Pa), and energy (joule, J) can be expressed in terms of base units. In calculations, units should be carried along with the numbers. Prefixes such as kilo- and milli- are used to denote multiples of units. Common expressions of concentration are molarity (moles of solute per liter of solution), molality (moles of solute per kilogram of solvent), formal concentration (formula units per liter), percent composition, and parts per million. To calculate quantities of reagents needed to prepare solutions, the relation $M_{conc} \cdot V_{conc} = M_{dil} \cdot V_{dil}$ is useful because it equates the moles of reagent removed from a stock solution to the moles delivered into a new solution. You should be able to use stoichiometry relations to calculate required masses or volumes of reagents for chemical reactions. From the mass of the product of a reaction, you should be able to compute how much reactant was consumed.

Exercises

The difference between *Exercises* and *Problems* is that complete solutions to *Exercises* are provided at the back of the book, whereas only numerical answers to *Problems* are provided. Complete solutions to *Problems* are in the *Solutions Manual.* Exercises usually cover most of the major ideas in each chapter in the minimum number of questions.

1-A. A solution with a final volume of 500.0 mL was prepared by dissolving 25.00 mL of methanol (CH_3OH, density = 0.791 4 g/mL) in chloroform.
(a) Calculate the *molarity* of methanol in the solution.
(b) The solution has a density of 1.454 g/mL. Find the *molality* of methanol.

1-B. A 48.0 wt% solution of HBr in water has a density of 1.50 g/mL.
(a) Find the formal concentration of HBr.
(b) What mass of solution contains 36.0 g of HBr?
(c) What volume of solution contains 233 mmol of HBr?
(d) How much solution is required to prepare 0.250 L of 0.160 M HBr?

1-C. A solution contains 12.6 ppm of dissolved $Ca(NO_3)_2$ (which dissociates into $Ca^{2+} + 2NO_3^-$). Find the concentration of NO_3^- in parts per million.

Problems

Units and Conversions

1-1. (a) List the SI units of length, mass, time, electric current, temperature, and amount of substance; write the abbreviation for each. (b) Write the units and symbols for frequency, force, pressure, energy, and power.

1-2. Write the names and abbreviations for each of the prefixes from 10^{-24} to 10^{24}. Which abbreviations are capitalized?

1-3. Write the name and number represented by each symbol. For example, for kW you should write kW = kilowatt = 10^3 watts.
(a) mW
(b) pm
(c) kΩ
(d) μF
(e) TJ
(f) ns
(g) fg
(h) dPa

. Express the following quantities with abbreviations for units d prefixes from Tables 1-1 through 1-3:

) 10^{-13} joules
) $4.317\,28 \times 10^{-8}$ farads
) $2.997\,9 \times 10^{14}$ hertz
(d) 10^{-10} meters
(e) 2.1×10^{13} watts
(f) 48.3×10^{-20} moles

5. During the 1980s, the average emission of carbon from burning ssil fuels on Earth was 5.4 petagrams (Pg) of carbon per year in e form of CO_2.[3]

) How many kg of C were placed in the atmosphere each year?
) How many kg of CO_2 were placed in the atmosphere each year?
) A metric ton is 1 000 kg. How many metric tons of CO_2 were aced in the atmosphere each year? If there were 5 billion people n Earth, how many tons of CO_2 were produced for each person?

-6. How many joules per second and how many calories per hour re produced by a 100.0-horsepower engine?

-7. A 120-pound woman working in an office consumes about $.2 \times 10^3$ kcal/day, whereas the same woman climbing a mountain eeds 3.4×10^3 kcal/day.

a) Express these numbers in terms of joules per second per kilo-gram of body mass (= watts per kilogram).
b) Which consumes more power (watts), the office worker or a 00-W light bulb?

1-8. (a) Refer to Table 1-4 and find how many meters are in 1 inch. How many inches are in 1 m?
(b) A mile contains 5 280 feet and a foot contains 12 inches. The speed of sound in the atmosphere at sea level is 345 m/s. Express the speed of sound in miles per second and miles per hour.
(c) There is a delay between lightning and thunder in a storm, because light reaches us almost instantaneously, but sound is slower. How many meters, kilometers, and miles away is a light-ning bolt if the sound reaches you 3.00 s after the light?

1-9. How many joules per second (J/s) are used by a device that requires 5.00×10^3 British thermal units per hour (Btu/h)? How many watts (W) does this device use?

1-10. Newton's law states that force = mass × acceleration. You also know that energy = force × distance and pressure = force/area. From these relations, derive the dimensions of newtons, joules, and pascals in terms of the fundamental SI units in Table 1-1. Check your answers in Table 1-2.

1-11. Dust falls on Chicago at a rate of 65 mg m^{-2} day^{-1}. Major metallic elements in the dust include Al, Mg, Cu, Zn, Mn, and Pb.[4] Pb accumulates at a rate of 0.03 mg m^{-2} day^{-1}. How many metric tons (1 metric ton = 1 000 kg) of Pb fall on the 535 square kilometers of Chicago in 1 year?

Chemical Concentrations

1-12. Define the following terms:

(a) molarity
(b) molality
(c) density
(d) weight percent
(e) volume percent
(f) parts per million
(g) parts per billion
(h) formal concentration

1-13. Why is it more accurate to say that the concentration of a solution of acetic acid is 0.01 F rather than 0.01 M? (Despite this distinction, we will usually write 0.01 M.)

1-14. What is the formal concentration (expressed as mol/L = M) of NaCl when 32.0 g are dissolved in water and diluted to 0.500 L?

1-15. How many grams of methanol (CH_3OH, FM 32.04) are contained in 0.100 L of 1.71 M aqueous methanol (that is, 1.71 mol CH_3OH/L solution)?

1-16. The concentration of a gas is related to its pressure by the *ideal gas law:*

$$\text{Concentration}\left(\frac{\text{mol}}{\text{L}}\right) = \frac{n}{V} = \frac{P}{RT}$$

$$R = \text{gas constant} = 0.083\,14\,\frac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}}$$

where n is the number of moles, V is volume (L), P is pressure (bar), and T is temperature (K).
(a) The maximum pressure of ozone in the Antarctic stratosphere in Figure 1-1 is 19 mPa. Convert this pressure into bars.
(b) Find the molar concentration of ozone in part **(a)** if the temperature is −70° C.

1-17. Any dilute aqueous solution has a density near 1.00 g/mL. Suppose the solution contains 1 ppm of solute; express the concentration of solute in g/L, μg/L, μg/mL, and mg/L.

1-18. The concentration of the alkane $C_{20}H_{42}$ (FM 282.55) in a particular sample of rainwater is 0.2 ppb. Assume that the density of rainwater is close to 1.00 g/mL and find the molar concentration of $C_{20}H_{42}$.

1-19. How many grams of perchloric acid, $HClO_4$, are contained in 37.6 g of 70.5 wt% aqueous perchloric acid? How many grams of water are in the same solution?

1-20. The density of 70.5 wt% aqueous perchloric acid is 1.67 g/mL. Recall that grams refers to grams of *solution* (= g $HClO_4$ + g H_2O).
(a) How many grams of solution are in 1.000 L?
(b) How many grams of $HClO_4$ are in 1.000 L?
(c) How many moles of $HClO_4$ are in 1.000 L?

1-21. An aqueous solution containing 20.0 wt% KI has a density of 1.168 g/mL. Find the molality (m, not M) of the KI solution.

1-22. A cell in your adrenal gland has about 2.5×10^4 tiny compartments called *vesicles* that contain the hormone epinephrine (also called adrenaline).
(a) An entire cell has about 150 fmol of epinephrine. How many attomoles (amol) of epinephrine are in each vesicle?
(b) How many molecules of epinephrine are in each vesicle?
(c) The volume of a sphere of radius r is $\frac{4}{3}\pi r^3$. Find the volume of a spherical vesicle of radius 200 nm. Express your answer in cubic meters (m^3) and liters, remembering that 1 L = 10^{-3} m^3.
(d) Find the molar concentration of epinephrine in the vesicle if it contains 10 amol of epinephrine.

1-23. The concentration of sugar (glucose, $C_6H_{12}O_6$) in human blood ranges from about 80 mg/100 mL before meals to 120 mg/100 mL after eating. Find the molarity of glucose in blood before and after eating.

1-24. An aqueous solution of antifreeze contains 6.067 M ethylene glycol ($HOCH_2CH_2OH$, FM 62.07) and has a density of 1.046 g/mL.
(a) Find the mass of 1.000 L of this solution and the number of grams of ethylene glycol per liter.
(b) Find the molality of ethylene glycol in this solution.

1-25. Protein and carbohydrates provide 4.0 Cal/g, whereas fat gives 9.0 Cal/g. (Remember that 1 Calorie, with a capital C, is really 1 kcal.) The weight percents of these components in some foods are

Food	Wt% protein	Wt% carbohydrate	Wt% fat
Shredded wheat	9.9	79.9	—
Doughnut	4.6	51.4	18.6
Hamburger (cooked)	24.2	—	20.3
Apple	—	12.0	—

Calculate the number of calories per gram and calories per ounce in each of these foods. (Use Table 1-4 to convert grams into ounces, remembering that there are 16 ounces in 1 pound.)

1-26. It is recommended that drinking water contain 1.6 ppm fluoride (F^-) for prevention of tooth decay. Consider a reservoir with a diameter of 4.50×10^2 m and a depth of 10.0 m. (The volume is $\pi r^2 h$, where r is the radius and h is the height.) How many grams of F^- should be added to give 1.6 ppm? How many grams of sodium fluoride, NaF, contain this much fluoride?

1-27. Noble gases (Group 18 in the periodic table) have the following volume concentrations in dry air: He, 5.24 ppm; Ne, 18.2 ppm; Ar, 0.934%; Kr, 1.14 ppm; Xe, 87 ppb.
(a) A concentration of 5.24 ppm He means 5.24 μL of He per liter of air. Using the ideal gas law in Problem 1-16, find how many moles of He are contained in 5.24 μL at 25.00°C (298.15 K) and 1.000 bar. This number is the molarity of He in the air.
(b) Find the molar concentrations of Ar, Kr, and Xe in air at 25°C and 1 bar.

Preparing Solutions

1-28. How many grams of boric acid, $B(OH)_3$ (FM 61.83), should be used to make 2.00 L of 0.050 0 M solution? What kind of flask is used to prepare this solution?

1-29. Describe how you would prepare approximately 2 L of 0.050 0 m boric acid, $B(OH)_3$.

1-30. What is the maximum volume of 0.25 M sodium hypochlorite solution (NaOCl, laundry bleach) that can be prepared by dilution of 1.00 L of 0.80 M NaOCl?

1-31. How many grams of 50 wt% NaOH (FM 40.00) should be diluted to 1.00 L to make 0.10 M NaOH? (Answer with two digits.)

1-32. A bottle of concentrated aqueous sulfuric acid, labeled 98.0 wt% H_2SO_4, has a concentration of 18.0 M.
(a) How many milliliters of reagent should be diluted to 1.000 L to give 1.00 M H_2SO_4?
(b) Calculate the density of 98.0 wt% H_2SO_4.

1-33. What is the density of 53.4 wt% aqueous NaOH (FM 40.00) if 16.7 mL of the solution diluted to 2.00 L gives 0.169 M NaOH?

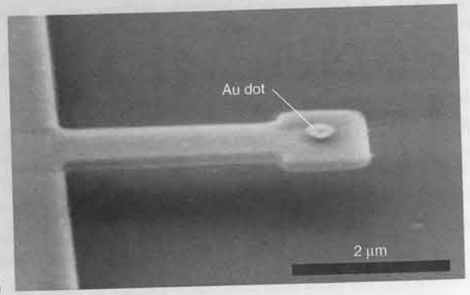
Stoichiometry Calculations

1-34. How many milliliters of 3.00 M H_2SO_4 are required to react with 4.35 g of solid containing 23.2 wt% $Ba(NO_3)_2$ if the reaction is $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4(s)$?

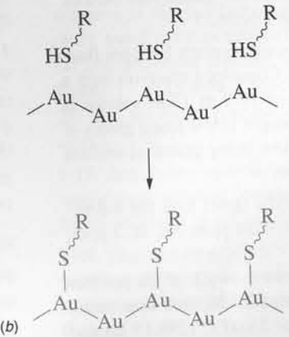
1-35. How many grams of 0.491 wt% aqueous HF are required to provide a 50% excess to react with 25.0 mL of 0.023 6 M Th^{4+} by the reaction $Th^{4+} + 4F^- \rightarrow ThF_4(s)$?

2 Tools of the Trade

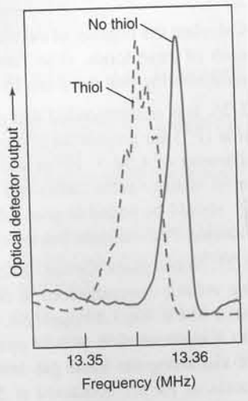
THE SMALLEST BALANCES



(a)

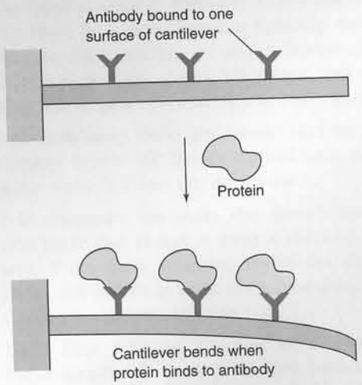


(b)



(c)

(a) Silicon cantilever with gold dot deposited on the surface, *(b)* Organic compound with thiol (—SH) group at the end binds to gold surface. *(c)* Resonant vibrational frequency of cantilever changes when thiol compound binds to gold dot. *[B. Ilic, H. G. Craighead, S. Krylov, W. Senaratne, C. Ober, and P. Neuzil, "Attogram Detection Using Nanoelectromechanical Oscillators," J. Appl. Phys. **2004**, 95, 3694.]*



Binding of molecules to one side creates surface stress that bends the cantilever.

Scientists can fabricate *microelectromechanical devices* such as the *cantilever* above, which is a beam of silicon anchored at one end. The beam has a resonant vibrational frequency near 13×10^6 hertz (13 MHz) when stimulated with a *piezoelectric* vibrator. (A *piezoelectric* crystal, such as quartz, is one whose dimensions change in response to an electric field.) When 93 attograms (93×10^{-18} *g*) of an organic compound bind to the gold dot near the end of the cantilever, the vibrational frequency decreases by 3.5 kHz because of the extra mass on the beam. The minimum mass that can be detected is estimated as 0.4 attogram.

Microcantilevers can be coated with DNA or antibodies to respond to biological molecules or even a single virus.[1,2,3] Bound material can be detected by the change in resonant frequency, as above, or by measuring nanometer-scale static bending, shown at the left, caused by stress on the surface of the cantilever when molecules bind.

Analytical chemistry extends from simple "wet" chemical procedures to elaborate instrumental methods. This chapter describes basic laboratory apparatus and manipulations associated with chemical measurements. We also introduce spreadsheets, which have become essential to everyone who manipulates quantitative data.

2-1 Safe, Ethical Handling of Chemicals and Waste

Chemical experimentation, like driving a car or operating a household, creates hazards. *The primary safety rule is to familiarize yourself with the hazards and then to do nothing that you (or your instructor or supervisor) consider to be dangerous.* If you believe that an operation is hazardous, discuss it first and do not proceed until sensible precautions are in place.

Preservation of a habitable planet demands that we minimize waste production and responsibly dispose of waste that is generated (Box 2-1). Recycling of chemicals is practiced in industry for economic as well as ethical reasons; it should be an important component of pollution control in your lab.

Before working, familiarize yourself with safety features of your laboratory. You should wear goggles or safety glasses with side shields (Figure 2-1) at all times in the lab to protect your eyes from liquids and glass, which fly around when least expected. Contact lenses are not recommended in the lab, because vapors can be trapped between the lens and your eye. You can protect your skin from spills and flames by wearing a flame-resistant lab coat. Use rubber gloves when pouring concentrated acids. Do not eat or drink in the lab.

Organic solvents, concentrated acids, and concentrated ammonia should be handled in a fume hood. Air flowing into the hood keeps fumes out of the lab and dilutes the fumes before expelling them from the roof. Never generate large quantities of toxic fumes that are allowed to escape through the hood. Wear a respirator when handling fine powders, which could produce a cloud of dust that might be inhaled.

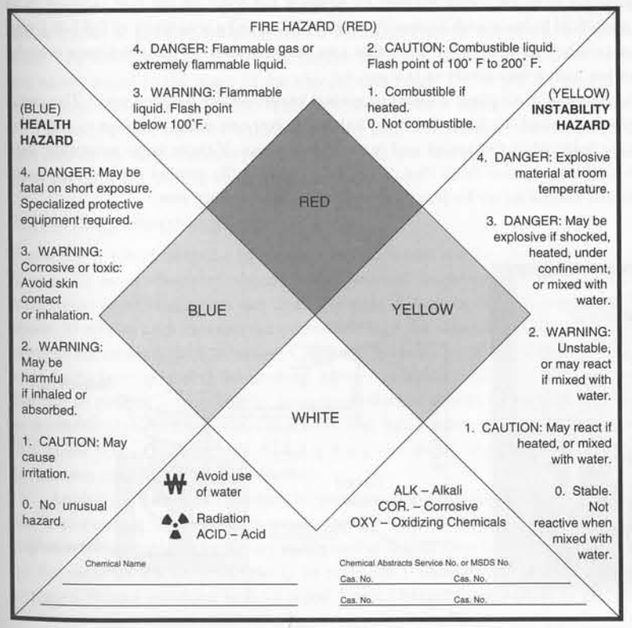
Box 2-1 Disposal of Chemical Waste

If carelessly discarded, many laboratory and household chemicals and products are harmful to plants, animals, and people.[4] For each experiment, your instructor should establish procedures for waste disposal. Options include (1) pouring solutions down the drain and diluting with tap water, (2) saving the waste for disposal in an approved landfill, (3) treating waste to decrease the hazard and then pouring it down the drain or saving it for a landfill, and (4) recycling. *Chemically incompatible wastes should never be mixed with each other, and each waste container must be labeled to indicate the quantity and identity of its contents.* Waste containers must indicate whether the contents are flammable, toxic, corrosive, or reactive, or have other dangerous properties.

A few examples illustrate different approaches to managing lab waste.[5] Dichromate ($Cr_2O_7^{2-}$) is reduced to Cr^{3+} with sodium hydrogen sulfite ($NaHSO_3$), treated with hydroxide to make insoluble $Cr(OH)_3$, and evaporated to dryness for disposal in a landfill. Waste acid is mixed with waste base until nearly neutral (as determined with pH paper) and then poured down the drain. Waste iodate (IO_3^-) is reduced to I^- with $NaHSO_3$, neutralized with base, and poured down the drain. Waste Pb^{2+} solution is treated with sodium metasilicate (Na_2SiO_3) solution to precipitate insoluble $PbSiO_3$ that can be packaged for a landfill. Waste silver or gold is treated to recover the metal.[6] Toxic gases used in a fume hood are bubbled through a chemical trap or burned to prevent escape from the hood.

Limitations of gloves: In 1997, popular Dartmouth College chemistry professor Karen Wetterhahn, age 48, died from a drop of dimethylmercury absorbed through the latex rubber gloves she was wearing. Many organic compounds readily penetrate rubber. Wetterhahn was an expert in the biochemistry of metals and the first female professor of chemistry at Dartmouth. She was a mother of two children and played a major role in bringing more women into science and engineering.

Figure 2-1 Goggles or safety glasses with side shields should be worn at all times in every lab. *[Stockdisk.]*



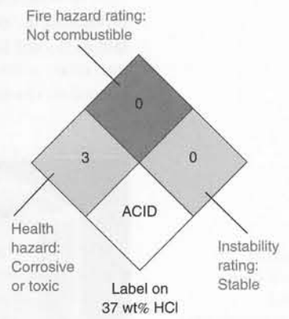


Figure 2-2 Chemical hazards label used by the National Fire Protection Association.

Clean up spills immediately to prevent accidental contact by the next person who comes along. Treat spills on your skin first by flooding with water. In anticipation of splashes on your body or in your eyes, know where to find and how to operate the emergency shower and eyewash. If the sink is closer than an eyewash, use the sink first for splashes in your eyes. Know how to operate the fire extinguisher and how to use an emergency blanket to extinguish burning clothing. A first aid kit should be available, and you should know how and where to seek emergency medical assistance.

Label all vessels to indicate what they contain. An unlabeled bottle left and forgotten in a refrigerator or cabinet presents an expensive disposal problem, because the contents must be analyzed before they can be legally discarded. National Fire Protection Association labels shown in Figure 2-2 identify hazards associated with chemical reagents. A Material Safety Data Sheet provided with each chemical sold in the United States lists hazards and safety precautions for that chemical. It gives first aid procedures and instructions for handling spills.

2-2 The Lab Notebook

he lab notebook must
State what was done
State what was observed
Be understandable to someone else

The critical functions of your lab notebook are to state *what you did* and *what you observed,* and it should be *understandable by a stranger.* The greatest error, made even by experienced scientists, is writing incomplete or unintelligible notebooks. Using *complete sentences* is an excellent way to prevent incomplete descriptions.

Beginning students often find it useful to write a complete description of an experiment, with sections dealing with purpose, methods, results, and conclusions. Arranging a notebook to accept numerical data prior to coming to the lab is an excellent way to prepare for an experiment. It is good practice to write a balanced chemical equation for every reaction you use. This practice helps you understand what you are doing and may point out what you do not understand about what you are doing.

The measure of scientific "truth" is the ability of different people to reproduce an experiment. A good lab notebook will state everything that was done and what you observed and will allow you or anyone else to repeat the experiment.

Record in your notebook the names of computer files where programs and data are stored. Paste hard copies of important data into your notebook. The lifetime of a printed page is an order of magnitude (or more) greater than the lifetime of a computer disk.

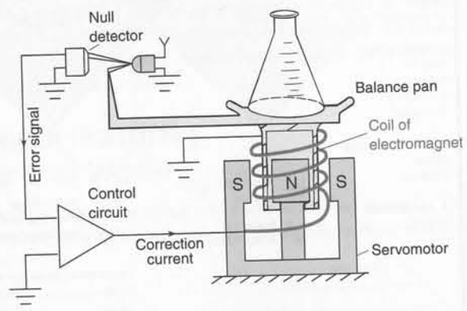
One fine future day, you or one of your classmates will make an important discovery and will seek a patent. The lab notebook is your legal record of your discovery. For this purpose, each page in your notebook should be signed and dated. Anything of potential importance should also be signed and dated by a second person.

2-3 Analytical Balance

An *electronic balance* uses an electromagnet to balance the load on the pan. Figure 2-3a shows a typical analytical balance with a capacity of 100–200 g and a sensitivity of 0.01–0.1 mg. *Sensitivity* is the smallest increment of mass that can be measured. A *microbalance* weighs milligram quantities with a sensitivity of 0.1 μg.

To weigh a chemical, first place a clean receiving vessel on the balance pan.[7] The mass of the empty vessel is called the **tare.** On most balances, you can press a button to reset the tare to 0. Add the chemical to the vessel and read its new mass. If there is no automatic tare operation, subtract the tare mass from that of the filled vessel. To protect the balance from corrosion, *chemicals should never be placed directly on the weighing pan.*

(a)



(b)

Figure 2-3 (*a*) Electronic analytical balance measures mass down to 0.1 mg. *[Courtesy Fisher Scientific, Pittsburgh, PA.]* (*b*) Displacement of the balance pan generates a correction current. The electromagnet then restores the pan to its initial position. N and S are the north and south poles of the permanent magnet. *[R. M. Schoonover, "A Look at the Electronic Analytical Balance," Anal. Chem. **1982,** 54, 973A. See also B. B. Johnson and J. D. Wells, "Cautions Concerning Electronic Analytical Balances," J. Chem. Ed. **1986,** 63, 86.]*

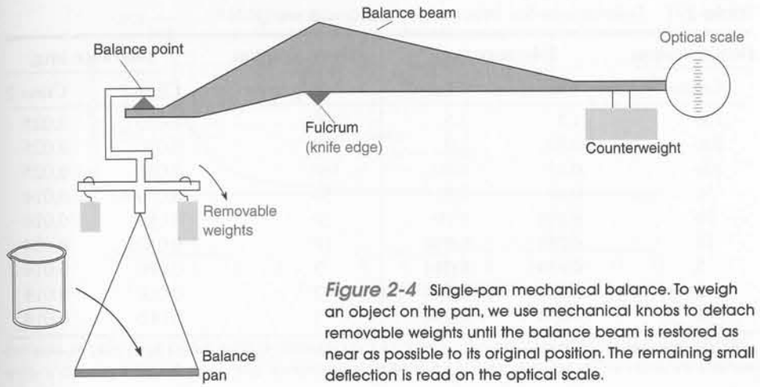


Figure 2-4 Single-pan mechanical balance. To weigh an object on the pan, we use mechanical knobs to detach removable weights until the balance beam is restored as near as possible to its original position. The remaining small deflection is read on the optical scale.

Weighing by difference

An alternate procedure, called "weighing by difference," is necessary for **hygroscopic** reagents, which rapidly absorb moisture from the air. First weigh a capped bottle containing dry reagent. Then quickly pour some reagent from that weighing bottle into a receiver. Cap the weighing bottle and weigh it again. The difference is the mass of reagent delivered from the weighing bottle. With an electronic balance, set the initial mass of the weighing bottle to zero with the tare button. Then deliver reagent from the bottle and reweigh the bottle. The negative reading on the balance is the mass of reagent delivered from the bottle.[8]

Principle of Operation

An object placed on the pan of the balance in Figure 2-3b pushes the pan down with a force equal to $m \times g$, where m is the mass of the object and g is the acceleration of gravity. The null detector senses the displacement and sends an error signal to the circuit that generates a correction current. This current flows through the coil beneath the pan, thereby creating a magnetic field that is repelled by a permanent magnet under the pan. As the deflection decreases, the output of the null detector decreases. The current required to restore the pan to its initial position is proportional to the mass on the pan.

The older single-pan *mechanical balance* shown in Figure 2-4 uses standard masses and a balance beam suspended on a sharp *knife edge* to measure the mass of the object on the balance pan. The mass of the pan hanging from the balance point (another knife edge) at the left is balanced by a counterweight at the right. An object placed on the pan pushes it down. We rotate knobs to remove weights from a bar that is above the pan and hidden inside the balance. The balance beam is restored almost to its original position when the masses removed are nearly equal to the mass of the object on the pan. The slight difference from the original position is shown on an optical scale, whose reading is added to that of the knobs.

A mechanical balance should be in its arrested position when you load or unload the pan and in the half-arrested position when you are dialing weights. This practice minimizes wear on the knife edges, which degrades sensitivity.

Preventing Weighing Errors

Use a paper towel or tissue to handle the vessel you are weighing, because fingerprints will change its mass. Samples should be at *ambient temperature* (the temperature of the surroundings) to prevent errors due to air currents. A sample that has been dried in an oven takes about 30 min to cool to room temperature. Place the sample in a desiccator during cooling to prevent accumulation of moisture. Close the glass doors of the balance in Figure 2-3a to prevent drafts from affecting the reading. Many top-loading balances have a plastic fence around the pan to protect it from drafts. Sensitive balances should be located on a heavy table, such as a marble slab, to minimize vibrations. The balance has adjustable feet and a bubble meter that allow you to keep it level. Avoid spilling chemicals into the gap between the coil and the permanent magnet of the servomotor.

Analytical balances calibrate themselves automatically by placing a standard mass on the load-bearing structure and measuring the current required to balance the weight. Less expensive electronic balances are calibrated at the factory, where the force of gravity may not be the same as the force of gravity in your lab. (Gravitational acceleration varies by ≈0.1% among different locations in the United States.) Magnetic materials or electromagnetic fields

Table 2-1 Tolerances for laboratory balance weights[a]

Denomination	Tolerance (mg)		Denomination	Tolerance (mg)	
Grams	Class 1	Class 2	Milligrams	Class 1	Class 2
500	1.2	2.5	500	0.010	0.025
200	0.50	1.0	200	0.010	0.025
100	0.25	0.50	100	0.010	0.025
50	0.12	0.25	50	0.010	0.014
20	0.074	0.10	20	0.010	0.014
10	0.050	0.074	10	0.010	0.014
5	0.034	0.054	5	0.010	0.014
2	0.034	0.054	2	0.010	0.014
1	0.034	0.054	1	0.010	0.014

a. Tolerances are defined in ASTM (American Society for Testing and Materials) Standard E 617. Classes 1 and 2 are the most accurate. Larger tolerances exist for Classes 3–6, which are not given in this table.

from neighboring instruments can affect the balance reading. Periodically check your balance by weighing a standard mass. *Tolerances* (allowable deviations) for standard masses are listed in Table 2-1.

Buoyancy

Your weight when swimming is nearly zero, which is why people can float. **Buoyancy** is the upward force exerted on an object in a liquid or gaseous fluid.[9] An object weighed in air appears lighter than its actual mass by an amount equal to the mass of air that it displaces. True mass is the mass measured in vacuum. A standard mass in a balance is also affected by buoyancy, so it weighs less in air than in vacuum. A buoyancy error occurs whenever the density of the object being weighed is not equal to the density of the standard mass.

If mass m' is read from a balance, the true mass m of the object weighed in vacuum is given by[10]

Buoyancy equation:

$$m = \frac{m'\left(1 - \frac{d_a}{d_w}\right)}{\left(1 - \frac{d_a}{d}\right)} \qquad (2\text{-}1)$$

where d_a is the density of air (0.001 2 g/mL near 1 bar and 25°C),[11] d_w is the density of the calibration weights (typically 8.0 g/mL), and d is the density of the object being weighed.

Example Buoyancy Correction

A pure compound called "tris" is used as a *primary standard* to measure concentrations of acids. The volume of acid required to react with a known mass of tris tells us the concentration of the acid. Find the true mass of tris (density = 1.33 g/mL) if the apparent mass weighed in air is 100.00 g.

Solution Assuming that the balance weights have a density of 8.0 g/mL and the density of air is 0.001 2 g/mL, we find the true mass by using Equation 2-1:

$$m = \frac{100.00\text{ g}\left(1 - \frac{0.001\,2\text{ g/mL}}{8.0\text{ g/mL}}\right)}{1 - \frac{0.001\,2\text{ g/mL}}{1.33\text{ g/mL}}} = 100.08\text{ g}$$

Unless we correct for buoyancy, we would think that the mass of tris is 0.08% less than the actual mass and we would think that the molarity of acid reacting with the tris is 0.08% less than the actual molarity.

Figure 2-5 shows buoyancy corrections for several substances. When you weigh water with a density of 1.00 g/mL, the true mass is 1.001 1 g when the balance reads 1.000 0 g. The

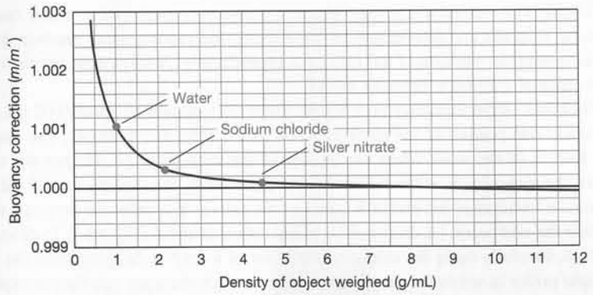


Figure 2-5 Buoyancy correction, assuming d_a = 0.001 2 g/mL and d_w = 8.0 g/mL. The apparent mass measured in air (1.000 0 g) is multiplied by the buoyancy correction to find the true mass.

error is 0.11%. For NaCl with a density of 2.16 g/mL, the error is 0.04%; and for $AgNO_3$ with a density of 4.45 g/mL, the error is only 0.01%.

2-4 Burets

The **buret** in Figure 2-6a is a precisely manufactured glass tube with graduations enabling you to measure the volume of liquid delivered through the stopcock (the valve) at the bottom. The 0-mL mark is near the top. If the initial liquid level is 0.83 mL and the final level is 27.16 mL, then you have delivered 27.16 − 0.83 = 26.33 mL. Class A burets (the most accurate grade) are certified to meet the tolerances in Table 2-2. If the reading of a 50-mL buret is 27.16 mL, the true volume can be anywhere in the range 27.21 to 27.11 mL and still be within the tolerance of ±0.05 mL.

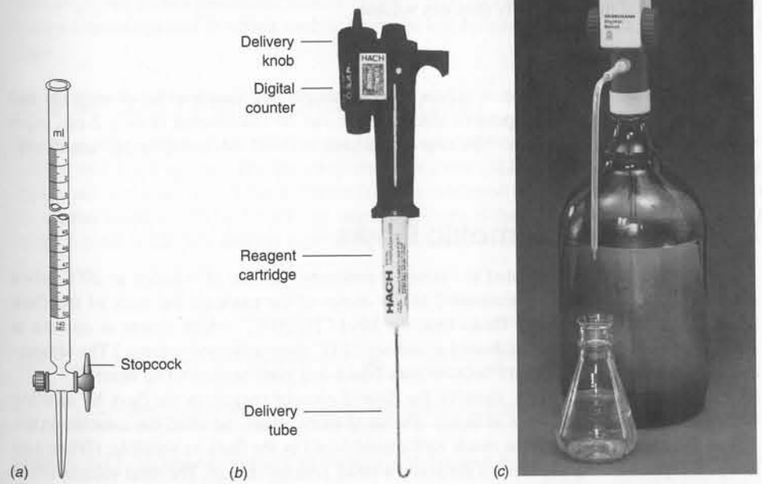
When reading the liquid level in a buret, your eye should be at the same height as the top of the liquid. If your eye is too high, the liquid seems to be higher than it really is. If your eye is too low, the liquid appears too low. The error that occurs when your eye is not at the same height as the liquid is called **parallax.**

The surface of most liquids forms a concave **meniscus** like that shown in Figure 2-7.[12] It is helpful to use black tape on a white card as a background for locating the precise position of the meniscus. Move the black strip up the buret to approach the meniscus. The bottom of the meniscus turns dark as the black strip approaches, thus making the meniscus more easily

Table 2-2 Tolerances of Class A burets

Buret volume (mL)	Smallest graduation (mL)	Tolerance (mL)
5	0.01	±0.01
10	0.05 *or* 0.02	±0.02
25	0.1	±0.03
50	0.1	±0.05
100	0.2	±0.10

Figure 2-6 (*a*) Glass buret. *[Courtesy A. H. Thomas Co., Philadelphia, PA.]* (*b*) Digital titrator with plastic cartridge containing reagent solution is used for analyses in the field. *[Courtesy Hach Co., Loveland, CO.]* (*c*) Battery-operated electronic buret with digital readout delivers 0.01-mL increments from a reagent bottle. This device can be used for accurate titrations in the field. *[Courtesy Cole-Parmer Co., Niles, IL.]*



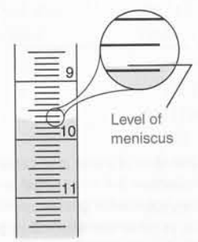
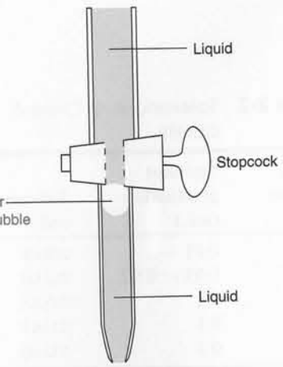


Figure 2-7 Buret with the meniscus at 9.68 mL. Estimate the reading of any scale to the nearest tenth of a division. This buret has 0.1-mL divisions, so we estimate the reading to the nearest 0.01 mL.

erating a buret:
Wash buret with new solution
liminate air bubble before use
rain liquid slowly
eliver fraction of a drop near end point
ead bottom of concave meniscus
stimate reading to 1/10 of a division
void parallax
ccount for graduation thickness in readings



igure 2-8 An air bubble trapped beneath he stopcock should be expelled before you se the buret.

recision refers to the reproducibility of replicate deliveries.
ccuracy refers to the difference between the stated volume and the actual volume delivered.

readable. Highly colored solutions may appear to have two meniscuses; either one may be used. Because volumes are determined by subtracting one reading from another, the important point is to read the position of the meniscus reproducibly. Always estimate the reading to the nearest tenth of a division between marks.

The thickness of the markings on a 50-mL buret corresponds to about 0.02 mL. For best accuracy, select one portion of the marking to be called zero. For example, you can say that the liquid level is *at* the mark when the bottom of the meniscus just touches the top of the mark. When the meniscus is at the *bottom* of the same mark, the reading is 0.02 mL greater.

For precise location of the end of a titration, we deliver less than one drop at a time from the buret near the end point. (A drop from a 50-mL buret is about 0.05 mL.) To deliver a fraction of a drop, carefully open the stopcock until part of a drop is hanging from the buret tip. (Some people prefer to rotate the stopcock rapidly through the open position to expel part of a drop.) Then touch the inside glass wall of the receiving flask to the buret tip to transfer the droplet to the wall of the flask. Carefully tip the flask so that the main body of liquid washes over the newly added droplet. Swirl the flask to mix the contents. Near the end of a titration, tip and rotate the flask often to ensure that droplets on the wall containing unreacted analyte contact the bulk solution.

Liquid should drain evenly down the wall of a buret. The tendency of liquid to stick to glass is reduced by draining the buret slowly (<20 mL/min). If many droplets stick to the wall, then clean the buret with detergent and a buret brush. If this cleaning is insufficient, soak the buret in peroxydisulfate–sulfuric acid cleaning solution,[13] which eats clothing and people, as well as grease in the buret. Never soak volumetric glassware in alkaline solutions, which attack glass. A 5 wt% NaOH solution at 95°C dissolves Pyrex glass at a rate of 9 μm/h.

Error can be caused by failure to expel the bubble of air often found directly beneath the stopcock (Figure 2-8). If the bubble becomes filled with liquid during the titration, then some volume that drained from the graduated portion of the buret did not reach the titration vessel. The bubble can be dislodged by draining the buret for a second or two with the stopcock wide open. You can expel a tenacious bubble by abruptly shaking the buret while draining it into a sink.

When you fill a buret with fresh solution, it is a wonderful idea to rinse the buret several times with small portions of the new solution, discarding each wash. It is not necessary to fill the buret with wash solution. Simply tilt the buret to allow all surfaces to contact the wash liquid. This same technique should be used with any vessel (such as a spectrophotometer cuvet or a pipet) that is reused without drying.

The *digital titrator* in Figure 2-6b is convenient for use in the field where samples are collected. The counter tells how much reagent has been dispensed. The precision of 1% is 10 times poorer than that of a glass buret, but many measurements do not require higher precision. The battery-operated *electronic buret* in Figure 2-6c fits on a reagent bottle and delivers up to 99.99 mL in 0.01-mL increments. For titrations requiring the very highest precision, measure the *mass* of reagent, instead of the volume, delivered from a buret or syringe.[14] Mass can be measured more precisely than can volume.

Microscale Titrations

"Microscale" student experiments reduce costs by decreasing consumption of reagents and generation of waste. An inexpensive student buret can be constructed from a 2-mL pipet graduated in 0.01-mL intervals.[15] Volume can be read to 0.001 mL and titrations can be carried out with a precision of 1%.

2-5 Volumetric Flasks

A **volumetric flask** is calibrated to contain a particular volume of solution at 20°C when the bottom of the meniscus is adjusted to the center of the mark on the neck of the flask (Figure 2-9, Table 2-3). Most flasks bear the label "TC 20°C," which means *to contain* at 20°C. (Pipets and burets are calibrated *to deliver,* "TD," their indicated volume.) The temperature of the container is relevant because both liquid and glass expand when heated.

To use a volumetric flask, dissolve the desired mass of reagent in the flask by swirling with *less* than the final volume of liquid. Then add more liquid and swirl the solution again. Adjust the final volume with as much well-mixed liquid in the flask as possible. (When two different liquids are mixed, there is generally a small volume change. The total volume is *not*

Thermal expansion of water and glass is discussed in Section 2-9. In contrast to older types of glass, volumetric glassware made of Pyrex, Kimax, or other low-expansion glass can be safely dried in an oven heated to at least 320°C without harm,[16] although there is rarely reason to go above 150°C.

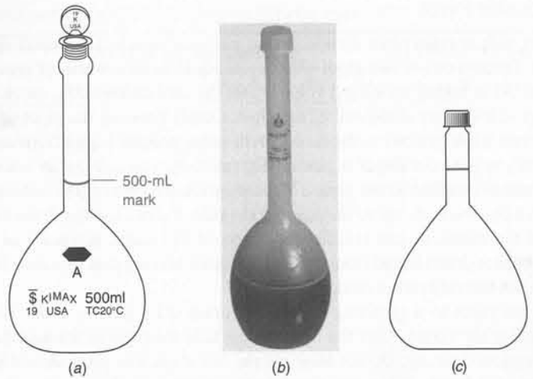


Figure 2-9 (*a*) Class A glass volumetric flask. *[Courtesy A. H. Thomas Co., Philadelphia, PA.]* (*b*) Class B polypropylene plastic volumetric flask for trace analysis. *[Courtesy Fisher Scientific, Pittsburgh, PA.]* Class A flasks meet tolerances of Table 2-3. Class B tolerances are twice as big as Class A tolerances. (*c*) Short-form volumetric flask with Teflon-lined screw cap fits in the analytical balance in Figure 2-3a. Teflon protects the cap from chemical attack.

Table 2-3 Tolerances of Class A volumetric flasks

Flask capacity (mL)	Tolerance (mL)
1	±0.02
2	±0.02
5	±0.02
10	±0.02
25	±0.03
50	±0.05
100	±0.08
200	±0.10
250	±0.12
500	±0.20
1 000	±0.30
2 000	±0.50

the sum of the two volumes that were mixed. By swirling the liquid in a nearly full volumetric flask before the liquid reaches the thin neck, you minimize the change in volume when the last liquid is added.) For good control, add the final drops of liquid with a pipet, *not a squirt bottle.* After adjusting the liquid to the correct level, hold the cap firmly in place and invert the flask several times to complete mixing. Before the liquid is homogeneous, we observe streaks (called *schliera*) arising from regions that refract light differently. After the schliera are gone, invert the flask a few more times to ensure complete mixing.

Figure 2-10 shows how liquid appears when it is at the *center* of the mark of a volumetric flask or a pipet. Adjust the liquid level while viewing the flask from above or below the level of the mark. The front and back of the mark describe an ellipse with the meniscus at the center.

Glass is notorious for *adsorbing* traces of chemicals—especially cations. **Adsorption** is the process in which a substance sticks to a surface. (In contrast, **absorption** is the process in which a substance is taken inside another, as water is taken into a sponge.) For critical work, you should **acid wash** glassware to replace low concentrations of cations on the surface with H^+. To do this, soak already thoroughly cleaned glassware in 3–6 M HCl (in a fume hood) for >1 h. Then rinse it well with distilled water and, finally, soak it in distilled water. Acid can be reused many times, as long as it is only used for clean glassware. Acid washing is *especially* appropriate for new glassware, which you should always assume is not clean. The polypropylene plastic volumetric flask in Figure 2-9b is designed for trace analysis (parts per billion concentrations) in which analyte might be lost by adsorption on the walls of a glass flask.

2-6 Pipets and Syringes

Pipets deliver known volumes of liquid. The *transfer pipet* in Figure 2-11a is calibrated to deliver one fixed volume. The last drop does not drain out of the pipet and *should not be blown out.* The *measuring pipet* in Figure 2-11b is calibrated like a buret. It is used to deliver a variable volume, such as 5.6 mL, by starting delivery at the 1.0-mL mark and terminating at the 6.6-mL mark. The transfer pipet is more accurate, with tolerances listed in Table 2-4.

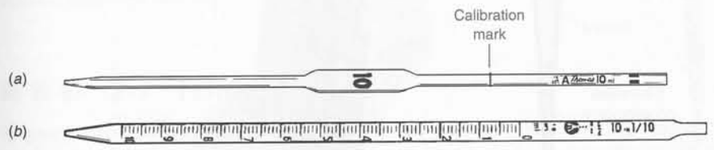


Figure 2-11 (*a*) Transfer pipet and (*b*) measuring (Mohr) pipet. *[Courtesy A. H. Thomas Co., Philadelphia, PA.]*

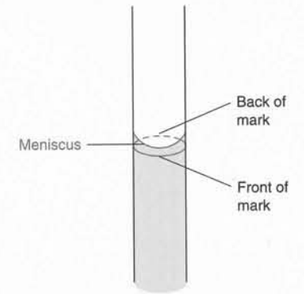


Figure 2-10 Proper position of the meniscus—at the center of the ellipse formed by the front and back of the calibration mark when viewed from above or below. Volumetric flasks and transfer pipets are calibrated to this position.

Table 2-4 Tolerances of Class A transfer pipets

Volume (mL)	Tolerance (mL)
0.5	±0.006
1	±0.006
2	±0.006
3	±0.01
4	±0.01
5	±0.01
10	±0.02
15	±0.03
20	±0.03
25	±0.03
50	±0.05
100	±0.08

o not blow the last drop out of a transfer
ipet.

Using a Transfer Pipet

Using a rubber bulb or other pipet suction device, *not your mouth,* suck liquid up past the calibration mark. Discard one or two pipet volumes of liquid to rinse traces of previous reagents from the pipet. After taking up a third volume past the calibration mark, quickly replace the bulb with your index finger at the end of the pipet. Gently pressing the pipet against the bottom of the vessel while removing the rubber bulb helps prevent liquid from draining below the mark while you put your finger in place. (Alternatively, you can use an automatic suction device that remains attached to the pipet.) Wipe the excess liquid off the outside of the pipet with a clean tissue. *Touch the tip of the pipet to the side of a beaker* and drain the liquid until the bottom of the meniscus just reaches the center of the mark, as shown in Figure 2-10. Touching the beaker draws liquid from the pipet without leaving part of a drop hanging when the liquid reaches the calibration mark.

Transfer the pipet to a receiving vessel and drain it by gravity *while holding the tip against the wall of the vessel.* After the liquid stops, hold the pipet to the wall for a few more seconds to complete draining. *Do not blow out the last drop.* The pipet should be nearly vertical at the end of delivery. When you finish with a pipet, you should rinse it with distilled water or soak it until you are ready to clean it. Solutions should never be allowed to dry inside a pipet because removing internal deposits is very difficult.

Micropipets

Micropipets (Figure 2-12) deliver volumes of 1 to 1 000 μL (1 μL = 10^{-6} L). Liquid is contained in the disposable polypropylene tip, which is stable to most aqueous solutions and many organic solvents except chloroform ($CHCl_3$). The tip is not resistant to concentrated nitric or sulfuric acids. To prevent aerosols from entering the pipet shaft, tips are available with polyethylene filters. Aerosols can corrode mechanical parts of the pipet or cross-contaminate biological experiments.

To use a micropipet, place a fresh tip tightly on the barrel. Keep tips in their package or dispenser so you do not contaminate the tips with your fingers. Set the desired volume with the knob at the top of the pipet. Depress the plunger to the first stop, which corresponds to the selected volume. Hold the pipet *vertically,* dip it 3–5 mm into the reagent solution, and

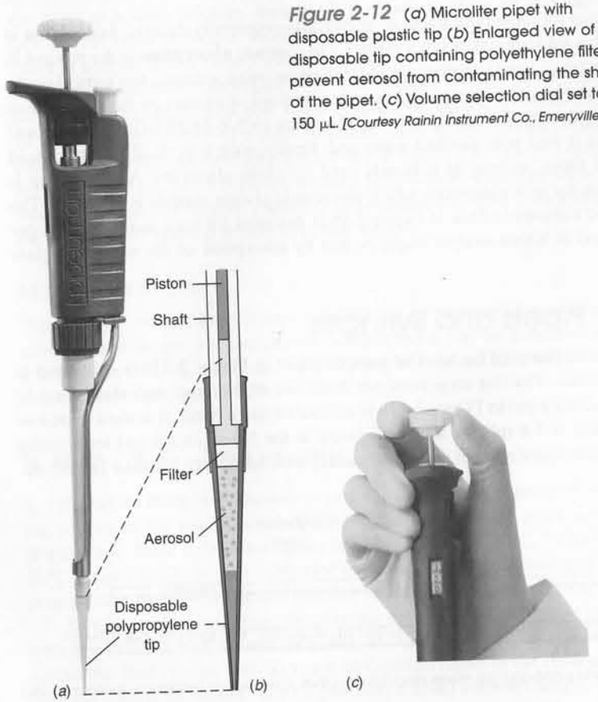


Figure 2-12 (*a*) Microliter pipet with disposable plastic tip (*b*) Enlarged view of disposable tip containing polyethylene filter to prevent aerosol from contaminating the shaft of the pipet. (*c*) Volume selection dial set to 150 μL. *[Courtesy Rainin Instrument Co., Emeryville, CA.]*

Table 2-5 Manufacturer's tolerances for micropipets

Pipet volume (μL)	At 10% of pipet volume		At 100% of pipet volume	
	Accuracy (%)	Precision (%)	Accuracy (%)	Precision (%)
Adjustable Pipets				
0.2–2	±8	±4	±1.2	±0.6
1–10	±2.5	±1.2	±0.8	±0.4
2.5–25	±4.5	±1.5	±0.8	±0.2
10–100	±1.8	±0.7	±0.6	±0.15
30–300	±1.2	±0.4	±0.4	±0.15
100–1 000	±1.6	±0.5	±0.3	±0.12
Fixed Pipets				
10			±0.8	±0.4
25			±0.8	±0.3
100			±0.5	±0.2
500			±0.4	±0.18
1 000			±0.3	±0.12

SOURCE: Data from Hamilton Co., Reno. NV.

slowly release the plunger to suck up liquid. The volume of liquid taken into the tip depends on the angle at which the pipet is held and how far beneath the liquid surface the tip is held during uptake. Withdraw the tip from the liquid by sliding it along the wall of the vessel to remove liquid from the outside of the tip. To dispense liquid, touch the tip to the wall of the receiver and gently depress the plunger to the first stop. Wait a few seconds to allow liquid to drain down the tip, and then depress the plunger further to squirt out the last liquid. Clean and wet a fresh tip by taking up and discarding two or three squirts of reagent. The tip can be discarded or rinsed well with a squirt bottle and reused. A tip with a filter (Figure 2-12b) cannot be cleaned for reuse.

Table 2-5 lists tolerances for micropipets from one manufacturer. As internal parts wear out, both precision and accuracy can decline by an order of magnitude. In a study[17] of 54 micropipets in use at a biomedical lab, 12 were accurate and precise to ≤1%. Five of 54 had errors ≥10%. When 54 quality control technicians at four pharmaceutical companies used a properly functioning micropipet, 10 people were accurate and precise to ≤1%. Six were inaccurate by ≥10%. Micropipets require periodic calibration and maintenance (cleaning, seal replacement, and lubrication) and operators require certification.[18]

Syringes

Microliter *syringes,* such as that in Figure 2-13, come in sizes from 1 to 500 μL and have an accuracy and precision near 1%. When using a syringe, take up and discard several volumes of liquid to wash the glass walls and to remove air bubbles from the barrel. The steel needle is attacked by strong acid and will contaminate strongly acidic solutions with iron.

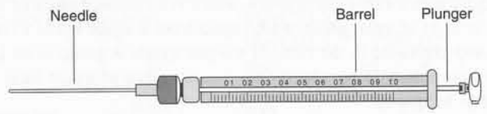


Figure 2-13 Hamilton syringe with a volume of 1 μL and divisions of 0.02 μL on the glass barrel. *[Courtesy Hamilton Co., Reno, NV.]*

2-7 Filtration

In *gravimetric analysis,* the mass of product from a reaction is measured to determine how much unknown was present. Precipitates from gravimetric analyses are collected by filtration, washed, and then dried. Most precipitates are collected in a *fritted-glass funnel* (also

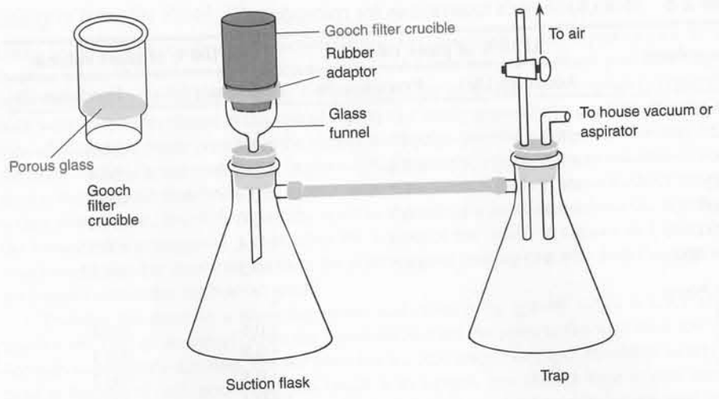


Figure 2-14 Filtration with a Gooch crucible that has a porous (*fritted*) glass disk through which liquid can pass. Suction can be applied by the house vacuum system or by an aspirator that uses flowing water to create vacuum. The trap prevents backup of tap water from the aspirator into the suction flask. Alternatively, the trap prevents liquid in your suction flask from being accidentally sucked into the house vacuum system. Using a trap is always a good idea, no matter what your source of vacuum.

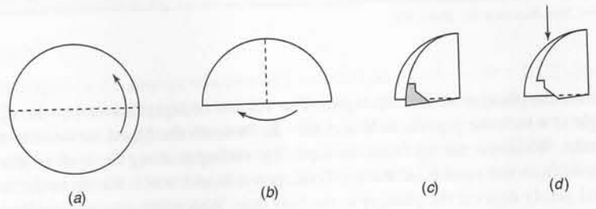


Figure 2-15 Folding filter paper for a conical funnel, (*a*) Fold the paper in half. (*b*) Then fold it in half again. (*c*) Tear off a corner to allow better seating of the paper in the funnel. (*d*) Open the side that was not torn when fitting the paper in the funnel.

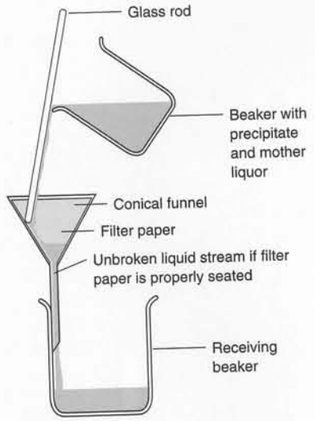


Figure 2-16 Filtering a precipitate. The conical funnel is supported by a metal ring attached to a ring stand, neither of which is shown.

Dust is a source of contamination in all experiments, so . . .

Cover all vessels whenever possible.

called a Gooch filter crucible) with suction applied to speed filtration (Figure 2-14). The porous glass plate in the funnel allows liquid to pass but retains solids. The empty funnel is first dried at 110°C and weighed. After collecting solid and drying again, the funnel and its contents are weighed a second time to determine the mass of collected solid. Liquid from which a substance precipitates or crystallizes is called the **mother liquor.** Liquid that passes through the filter is called **filtrate.**

In some gravimetric procedures, **ignition** (heating at high temperature over a burner or in a furnace) is used to convert a precipitate into a known, constant composition. For example, Fe^{3+} precipitates as hydrous ferric oxide, $FeOOH \cdot xH_2O$, with variable composition. Ignition converts it into pure Fe_2O_3 prior to weighing. When a precipitate is to be ignited, it is collected in **ashless filter paper,** which leaves little residue when burned.

To use filter paper with a conical glass funnel, fold the paper into quarters, tear off one corner (to allow a firm fit into the funnel), and place the paper in the funnel (Figure 2-15). The filter paper should fit snugly and be seated with some distilled water. When liquid is poured in, an unbroken stream of liquid should fill the stem of the funnel (Figure 2-16). The weight of liquid in the stem helps speed filtration.

For filtration, pour the slurry of precipitate down a glass rod to prevent splattering (Figure 2-16). (A **slurry** is a suspension of solid in liquid.) Particles adhering to the beaker or rod can be dislodged with a *rubber policeman,* which is a flattened piece of rubber at the end of a glass rod. Use a jet of appropriate wash liquid from a squirt bottle to transfer particles from the rubber and glassware to the filter. If the precipitate is going to be ignited, particles remaining in the beaker should be wiped onto a small piece of moist filter paper. Add that paper to the filter to be ignited.

2-8 Drying

Reagents, precipitates, and glassware are conveniently dried in an oven at 110°C. (Some chemicals require other temperatures.) *Anything that you put in the oven should be labeled.* Use a beaker and watchglass (Figure 2-17) to minimize contamination by dust during drying. It is good practice to cover all vessels on the benchtop to prevent dust contamination.

The mass of a gravimetric precipitate is measured by weighing a dry, empty filter crucible before the procedure and reweighing the same crucible filled with dry product after the procedure. To weigh the empty crucible, first bring it to "constant mass" by drying it in the

oven for 1 h or longer and then cooling it for 30 min in a desiccator. Weigh the crucible and then heat it again for about 30 min. Cool it and reweigh it. When successive weighings agree to ±0.3 mg, the filter has reached "constant mass." You can use a microwave oven instead of an electric oven for drying reagents and crucibles. Try an initial heating time of 4 min, with subsequent 2-min heatings. Use a 15-min cooldown before weighing.

A **desiccator** (Figure 2-18) is a closed chamber containing a drying agent called a **desiccant** (Table 2-6). The lid is greased to make an airtight seal and desiccant is placed in the bottom beneath the perforated disk. Another useful desiccant that is not in the table is 98% sulfuric acid. After placing a hot object in the desiccator, leave the lid cracked open for a minute until the object has cooled slightly. This practice prevents the lid from popping open when the air inside warms up. To open a desiccator, slide the lid sideways rather than trying to pull it straight up.

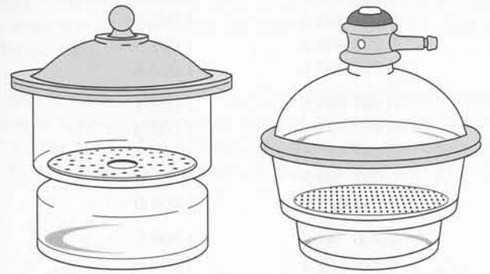


Figure 2-18 (*a*) Ordinary desiccator. (*b*) Vacuum desiccator that can be evacuated through the side arm at the top and then sealed by rotating the joint containing the side arm. Drying is more efficient at low pressure. *[Courtesy A. H. Thomas Co., Philadelphia, PA.]*

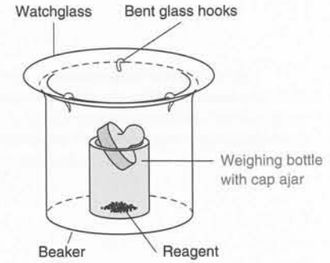


Figure 2-17 Use a watchglass as a dust cover while drying reagents or crucibles in the oven.

2-9 Calibration of Volumetric Glassware

Each instrument that we use has a scale of some sort to measure a quantity such as mass, volume, force, or electric current. Manufacturers usually certify that the indicated quantity lies within a certain *tolerance* from the true quantity. For example, a Class A transfer pipet is certified to deliver 10.00 ± 0.02 mL when you use it properly. Your individual pipet might always deliver 10.016 ± 0.004 mL in a series of trials. That is, your pipet delivers an average of 0.016 mL more than the indicated volume in repeated trials. **Calibration** is the process of measuring the actual quantity of mass, volume, force, electric current, and so on, that corresponds to an indicated quantity on the scale of an instrument.

Table 2-6 Efficiencies of drying agents

Agent	Formula	Water left in atmosphere (μg H_2O/L)[a]
Magnesium perchlorate, anhydrous	$Mg(ClO_4)_2$	0.2
"Anhydrone"	$Mg(ClO_4)_2 \cdot 1–1.5H_2O$	1.5
Barium oxide	BaO	2.8
Alumina	Al_2O_3	2.9
Phosphorus pentoxide	P_4O_{10}	3.6
Calcium sulfate (Drierite)[b]	$CaSO_4$	67
Silica gel	SiO_2	70

*a. Moist nitrogen was passed over each desiccant, and the water remaining in the gas was condensed and weighed. [A. I. Vogel, A Textbook of Quantitative Inorganic Analysis, 3rd ed. (New York: Wiley. 1961), p. 178.] For drying gases, the gas can be passed through a 60-cm-long Nafion tube. At 25°C, the residual moisture is 10 μg/L. If the drier is held at 0°C, the residual moisture is 0.8 μg/L. [K. J. Leckrone and J. M. Hayes. "Efficiency and Temperature Dependence of Water Removal by Membrane Dryers." Anal. Chem. **1997,** 69, 911.]*

*b. Used Drierite can be regenerated by irradiating 1.5-kg batches in a 100 × 190 mm Pyrex crystallizing dish in a microwave oven for 15 min. Stir the solid, heat a second time for 15 min. and place the hot, dry material back in its original container. Use small glass spacers between the crystallizing dish and the glass tray of the oven to protect the tray. [J. A. Green and R. W. Goetz, "Recycling Drierite," J. Chem. Ed. **1991,** 68, 429.]*

Table 2-7 Density of water

Temperature (°C)	Density (g/mL)	Volume of 1 g of water (mL)	
		At temperature shown[a]	Corrected to 20°C[b]
10	0.999 702 6	1.001 4	1.001 5
11	0.999 608 4	1.001 5	1.001 6
12	0.999 500 4	1.001 6	1.001 7
13	0.999 380 1	1.001 7	1.001 8
14	0.999 247 4	1.001 8	1.001 9
15	0.999 102 6	1.002 0	1.002 0
16	0.998 946 0	1.002 1	1.002 1
17	0.998 777 9	1.002 3	1.002 3
18	0.998 598 6	1.002 5	1.002 5
19	0.998 408 2	1.002 7	1.002 7
20	0.998 207 1	1.002 9	1.002 9
21	0.997 995 5	1.003 1	1.003 1
22	0.997 773 5	1.003 3	1.003 3
23	0.997 541 5	1.003 5	1.003 5
24	0.997 299 5	1.003 8	1.003 8
25	0.997 047 9	1.004 0	1.004 0
26	0.996 786 7	1.004 3	1.004 2
27	0.996 516 2	1.004 6	1.004 5
28	0.996 236 5	1.004 8	1.004 7
29	0.995 947 8	1.005 1	1.005 0
30	0.995 650 2	1.005 4	1.005 3

a. Corrected for buoyancy with Equation 2-1.

b. Corrected for buoyancy and expansion of borosilicate glass (0.001 0% K^{-1}).

ge 38 gives a detailed procedure for ibrating a buret.

For greatest accuracy, we calibrate volumetric glassware to measure the volume actually contained in or delivered by a particular piece of equipment. We do this by measuring the mass of water contained or delivered by the vessel and using the density of water to convert mass into volume.

In the most careful work, it is necessary to account for thermal expansion of solutions and glassware with changing temperature. For this purpose, you should know the lab temperature when a solution was prepared and when it is used. Table 2-7 shows that water expands 0.02% per degree near 20°C. Because the concentration of a solution is proportional to its density, we can write

Correction for thermal expansion:
$$\frac{c'}{d'} = \frac{c}{d} \qquad (2\text{-}2)$$

e concentration of the solution decreases en the temperature increases.

where c' and d' are the concentration and density at temperature T', and c and d apply at temperature T.

Example Effect of Temperature on Solution Concentration

A 0.031 46 M aqueous solution was prepared in winter when the lab temperature was 17°C. What is the molarity of the solution on a warm day when the temperature is 25°C?

Solution We assume that the thermal expansion of a dilute solution is equal to the thermal expansion of pure water. Then, using Equation 2-2 and densities from Table 2-7, we write

$$\frac{c' \text{ at } 25°}{0.997\,05 \text{ g/mL}} = \frac{0.031\,46 \text{ M}}{0.998\,78 \text{ g/mL}} \Rightarrow c' = 0.031\,41 \text{ M}$$

The concentration has decreased by 0.16% on the warm day.

Pyrex and other borosilicate glasses expand by 0.001 0% per degree near room temperature. If the temperature increases by 10°C, the volume of a piece of glassware increases by (10)(0.001 0%) = 0.010%. For most work, this expansion is insignificant.

To calibrate a 25-mL transfer pipet, you should first weigh an empty weighing bottle like the one in Figure 2-17. Then fill the pipet to the mark with distilled water, drain it into the weighing bottle, and cap the bottle to prevent evaporation. Weigh the bottle again to find the mass of water delivered from the pipet. Finally, use Equation 2-3 to convert mass into volume.

Small or odd-shaped vessels can be calibrated with Hg, which is easier than water to pour out of glass and is 13.6 times denser than water. This procedure is for researchers, not students.

$$\text{True volume} = (\text{grams of water}) \times (\text{volume of 1 g of } H_2O \text{ in Table 2-7}) \qquad (2\text{-}3)$$

Example Calibration of a Pipet

An empty weighing bottle had a mass of 10.313 g. After the addition of water from a 25-mL pipet, the mass was 35.225 g. If the lab temperature was 27°C, find the volume of water delivered by the pipet.

Solution The mass of water is 35.225 − 10.313 = 24.912 g. From Equation 2-3 and the next-to-last column of Table 2-7, the volume of water is (24.912 g)(1.004 6 mL/g) = 25.027 mL at 27°C. The last column in Table 2-7 tells us what the volume would be if the pipet were at 20°C. This pipet would deliver (24.912 g)(1.004 5 mL/g) = 25.024 mL at 20°C.

The pipet delivers less volume at 20°C than at 27°C because glass contracts slightly as the temperature is lowered. Volumetric glassware is usually calibrated at 20°C.

2-10 Introduction to Microsoft Excel

If you already use a spreadsheet, you can skip this section. The computer spreadsheet is an essential tool for manipulating quantitative information. In analytical chemistry, spreadsheets can help us with calibration curves, statistical analysis, titration curves, and equilibrium problems. Spreadsheets allow us to conduct "what if" experiments such as investigating the effect of a stronger acid or a different ionic strength on a titration curve. We use Microsoft Excel in this book as a tool for solving problems in analytical chemistry. Although you can skip over spreadsheets with no loss of continuity, spreadsheets will enrich your understanding of chemistry and provide a valuable tool for use outside this course.

This section introduces a few basic features of Excel 2000 for a PC computer. Other versions of Excel and other spreadsheets are not very different from what we describe. Excellent books are available if you want to learn much more about this software.[19]

Getting Started: Calculating the Density of Water

Let's prepare a spreadsheet to compute the density of water from the equation

$$\text{Density(g/mL)} = a_0 + a_1{*}T + a_2{*}T^2 + a_3{*}T^3 \qquad (2\text{-}4)$$

This equation is accurate to five decimal places over the range 4° to 40°C.

where T is temperature (°C) and $a_0 = 0.999\,89$, $a_1 = 5.332\,2 \times 10^{-5}$, $a_2 = -7.589\,9 \times 10^{-6}$, and $a_3 = 3.671\,9 \times 10^{-8}$.

The blank spreadsheet in Figure 2-19a has columns labeled A, B, C and rows numbered 1, 2, 3, . . . , 12. The box in column B, row 4 is called *cell* B4.

Begin each spreadsheet with a title to help make the spreadsheet more readable. In Figure 2-19b, we click in cell A1 and type "Calculating Density of H_2O with Equation 2-4". Then we click in cell A2 and write "(from the delightful book by Dan Harris)". The computer automatically spreads the text into adjoining cells.

We adopt a convention in this book in which constants are collected in column A. Type "Constants:" in cell A4. Then select cell A5 and type "a0=". Now select cell A6 and type the number 0.99989 (without extra spaces). In cells A7 to A12, enter the remaining constants. Powers of 10 are written, for example, as E-5 for 10^{-5}. Your spreadsheet should now look like Figure 2-19b.

Oops! I forgot one little trick. If you need more room in a column for the number of digits, you can grab the vertical line at the top of the column with your mouse and resize the column.

In cell B4, write the heading "Temp (°C)". Then enter temperatures from 5 through 40 in cells B5 through B12. This is our *input* to the spreadsheet. The *output* will be computed values of density in column C.

Columns

Rows

(a)

	A	B	C
1			
2			
3			
4		cell B4	
5			
6			
7			
8			
9			
10			
11			
12			

(b)

	A	B	C
1	Calculating Density of H2O with Equation 2-4		
2	(from the delightful book by Dan Harris)		
3			
4	Constants:		
5	a0 =		
6	0.99989		
7	a1 =		
8	5.3322E-05		
9	a2 =		
10	-7.5899E-06		
11	a3 =		
12	3.6719E-08		

(c)

	A	B	C
1	Calculating Density of H2O with Equation 2-4		
2	(from the delightful book by Dan Harris)		
3			
4	Constants:	Temp (°C)	Density (g/mL)
5	a0 =	5	0.99997
6	0.99989	10	
7	a1 =	15	
8	5.3322E-05	20	
9	a2 =	25	
10	-7.5899E-06	30	
11	a3 =	35	
12	3.6719E-08	40	

(d)

	A	B	C
1	Calculating Density of H2O with Equation 2-4		
2	(from the delightful book by Dan Harris)		
3			
4	Constants:	Temp (°C)	Density (g/mL)
5	a0 =	5	0.99997
6	0.99989	10	0.99970
7	a1 =	15	0.99911
8	5.3322E-05	20	0.99821
9	a2 =	25	0.99705
10	-7.5899E-06	30	0.99565
11	a3 =	35	0.99403
12	3.6719E-08	40	0.99223
13			
14	Formula:		
15	C5 = $A$6+$A$8*B5+$A$10*B5^2+$A$12*B5^3		

Figure 2-19 Evolution of a spreadsheet for computing the density of water.

Formulas begin with an equal sign. Arithmetic operations in a spreadsheet are

+	addition
-	subtraction
*	multiplication
/	division
^	exponentiation

Three kinds of entries:

label	A3 =
number	4.4E-05
formula	= $A$8*B5

In cell C4, enter the heading "Density (g/mL)". Cell C5 is the most important one in the table. In this one, you will write the *formula*

$$= \$A\$6 + \$A\$8*B5 + \$A\$10*B5\text{^}2 + \$A\$12*B5\text{^}3$$

(It doesn't matter whether or not you use spaces around the arithmetic operators.) When you hit RETURN, the number 0.99997 appears in cell C5. The formula above is the spreadsheet translation of Equation 2-4. $A$6 refers to the constant in cell A6. (We will explain the dollar signs shortly.) B5 refers to the temperature in cell B5. The times sign is * and the exponentiation sign is ^. For example, the term "$A$12*B5^3" means "(contents of cell A12) × (contents of cell B5)^3."

Now comes the most magical property of a spreadsheet. Highlight cell C5 and the empty cells below it from C6 to C12. Then select the FILL DOWN command from the EDIT menu. This procedure copies the formula from C5 into the cells below it and evaluates the numbers in each of the selected cells. The density of water at each temperature now appears in column C in Figure 2-19d.

In this example, we made three types of entries. *Labels* such as "a0=" were typed in as text. An entry that does not begin with a digit or an equal sign is treated as text. *Numbers,* such as 25, were typed in some cells. The spreadsheet treats a number differently from text. In cell C5, we entered a *formula* that necessarily begins with an equal sign.

Arithmetic Operations and Functions

Addition, subtraction, multiplication, division, and exponentiation have the symbols +, −, *, /, and ^. *Functions* such as Exp(·) can be typed by you or can be selected from the INSERT menu by choosing FUNCTION. Exp(·) raises e to the power in parentheses. Other functions such as Ln(·), Log(·), Sin(·), and Cos(·) are also available. In some spreadsheets, functions are written in all capital letters.

The order of arithmetic operations in formulas is negation first, followed by ^, followed by * and / (evaluated in order from left to right as they appear), finally followed by + and − (also evaluated from left to right). Make liberal use of parentheses to be sure that the computer does what you intend. The contents of parentheses are evaluated first, before carrying out operations outside the parentheses. Here are some examples:

$$9/5*100+32 = (9/5)*100+32 = (1.8)*100+32 = (1.8*100)+32 = (180)+32 = 212$$

$$9/5*(100+32) = 9/5*(132) = (1.8)*(132) = 237.6$$

$$9+5*100/32 = 9+(5*100)/32 = 9+(500)/32 = 9+(500/32) = 9+(15.625) = 24.625$$

$$9/5\text{^}2+32 = 9/(5\text{^}2)+32 = (9/25)+32 = (0.36)+32 = 32.36$$

$$-2\text{^}2 = 4 \quad \text{but} \quad -(2\text{^}2) = -4$$

When in doubt about how an expression will be evaluated, use parentheses to force what you intend.

Order of operations:
1. Negation (a minus sign before a term)
2. Exponentiation
3. Multiplication and division (in order from left to right)
4. Addition and subtraction (in order from left to right)

Operations within parentheses are evaluated first, from the innermost set.

Documentation and Readability

The first important *documentation* in the spreadsheet is the name of the file. A name such as "Expt 9 Gran Plot" is much more meaningful than "Dan's Lab". The next important feature is a title at the top of the spreadsheet, which tells its purpose. To remind ourselves what formulas were used in the spreadsheet, we added text (labels) at the bottom. In cell A14, write "Formula:" and in cell A15 write "C5 = $A$6+$A$8*B5+$A$10*B5^2+$A$12*B5^3". This documentation tells us how numbers in column C were calculated.

For additional readability in Figure 2-19, column C was set to display just five decimal places, even though the computer retains many more for its calculations. It does not throw away the digits that are not displayed. You can control the way numbers are displayed in a cell by going to the FORMAT menu, selecting CELLS, and going to the Number tab.

Documentation means labeling. If your spreadsheet cannot be read by another person without your help, it needs better documentation. (The same is true of your lab notebook!)

Absolute and Relative References

The formula "= $A$8*B5" refers to cells A8 and B5 in different manners. $A$8 is an *absolute reference* to the contents of cell A8. No matter where cell $A$8 is called from in the spreadsheet, the computer goes to cell A8 to look for a number. "B5" is a *relative reference* in the formula in cell C5. When called from cell C5, the computer goes to cell B5 to find a number. When called from cell C6, the computer goes to cell B6 to look for a number. If called from cell C19, the computer would look in cell B19. This is why the cell written without dollar signs is called a relative reference. If you want the computer to always look only in cell B5, then you should write "$B$5".

Absolute reference: $A$8
Relative reference: B5

Save your files frequently while you are working and make a backup file of anything that you don't want to lose.

2-11 Graphing with Microsoft Excel

Graphs are critical to understanding quantitative relations. Depending on which version of Excel you have, there may be some variation from what is described here.

To make a graph from the spreadsheet in Figure 2-19d, go to the INSERT menu and select CHART. A window appears with a variety of options. The one you will almost always want is XY (Scatter). Highlight XY (Scatter) and several options appear. Select the one that shows data points connected by a smooth curve. Click Next to move to the next window.

Now you are asked which cells contain the data to be plotted. Identify the *x* data by writing B5:B12 next to Data Range. Then write a comma and identify the *y* data by writing C5:C12. The input for Data Range now looks like B5:B12,C5:C12. Click the button to show that data are in columns, not rows. Click Next.

Now a small graph of your data appears. If it does not look as expected, make sure you selected the correct data, with *x* before *y*. The new window asks you for axis labels and an optional title for the graph. For the title, write "Density of Water" (without quotation marks). For the *x*-axis, enter "Temperature (°C)" and for the *y*-axis write "Density (g/mL)". Click Next.

Now you are given the option of drawing the graph on a new sheet or on the same sheet that is already open. For this case, select "As object in Sheet 1". Click Finish and the chart

	A	B	C	D	E	F	G	H
1	Calculating Density of H2O with Equation 2-4							
2	(from the delightful book by Dan Harris)							
3								
4	Constants:	Temp (°C)	Density (g/mL)					
5	a0 =	5	0.99997					
6	0.99989	10	0.99970					
7	a1 =	15	0.99911					
8	5.3322E-05	20	0.99821					
9	a2 =	25	0.99705					
10	-7.5899E-06	30	0.99565					
11	a3 =	35	0.99403					
12	3.6719E-08	40	0.99223					
13								
14	Formula:							
15	C5 = $A$6+$A$8*B5+$A$10*B5^2+$A$12*B5^3							
16								
17								

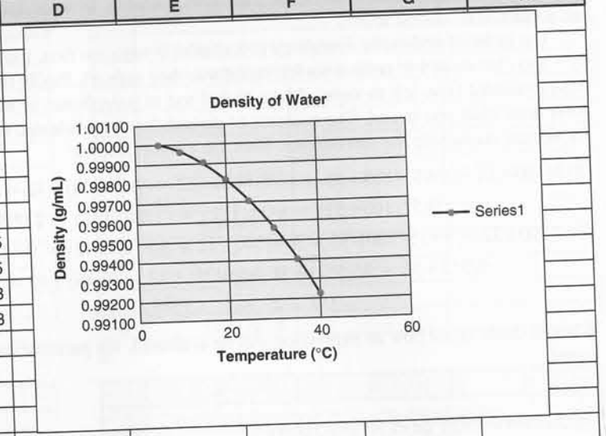


Figure 2-20 Initial density chart drawn by Excel.

will appear on your spreadsheet. Grab the chart with your mouse and move it to the right of the data in your spreadsheet, as shown in Figure 2-20.

You have just drawn your first graph! Excel gives us many options for changing features of the graph. Here are a few, but you should experiment with the graph to discover other formatting options. Double click on the *y*-axis and a window appears. Select the Patterns tab. Change Minor tic mark type from None to Outside and click OK. You will see new tic marks appear on the *y*-axis. Double click on the *y*-axis again and select the Number tab. Change the decimal places to 3 and click OK. Double click on the *y*-axis again and select the Scale tab. Set the minimum to 0.992 and the maximum to 1.000 and click OK.

Double click on the *x*-axis and select Patterns. Change the Minor tic mark type from None to Outside. Select Scale and set the maximum to 40, the major unit to 10, the minor unit to 5, and click OK.

Double click on the gray area of the graph and a window called Patterns appears. Select Automatic for the Border and None for the Area. This removes the gray background and gives a solid line around the graph. To add vertical lines at the major tic marks, select the graph with the mouse. Then go to the CHART menu and select CHART OPTIONS. In the window that appears, select Gridlines. For the Value (X) axis, check Major gridlines. Then select the tab for Legend and remove the check mark from Show Legend. The legend will disappear. Click OK. You should be getting the idea that you can format virtually any part of the chart.

Click on the outer border of the chart and handles appear. Grab the one on the right and resize the chart so it does not extend past column F of the spreadsheet. Grab the handle at the bottom and resize the chart so it does not extend below row 15. When you resized the chart, letters and numbers shrank. Double click on each set of numbers and change the font to 8 points. Double click on the labels and change the letters to 9 points. Your chart should now look like the one in Figure 2-21.

If you want to write on the chart, go to the VIEW menu and select TOOLBARS and DRAWING. Select the Text Box tool from the Drawing toolbar, click inside your chart, and you can begin typing words. You can move the words around and change their format. You can draw arrows on the chart with the Arrow tool. If you double click on a data point on the chart, a box appears that allows you to change the plotting symbols.

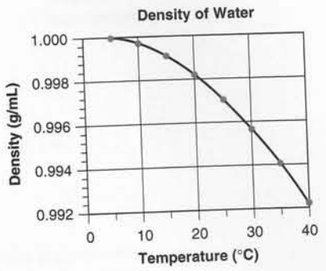


Figure 2-21 Density chart after reformatting.

Terms to Understand

absorption
acid wash
adsorption
ashless filter paper
buoyancy
buret
calibration
desiccant
desiccator
filtrate
hygroscopic
ignition
meniscus
mother liquor
parallax
pipet
slurry
tare
volumetric flask

Summary

Safety requires you to think in advance about what you will do; never do anything that seems dangerous. Know how to use safety equipment such as goggles, fume hood, lab coat, gloves, emergency shower, eyewash, and fire extinguisher. Chemicals should be stored and used in a manner that minimizes contact of solids, liquids, and vapors with people. Environmentally acceptable disposal procedures should be established in advance for every chemical that you use. Your lab notebook tells what you did and what you observed; it should be understandable to other people. It also should allow you to repeat an experiment in the same manner in the future. You should understand the principles of operation of electronic and mechanical balances and treat them as delicate equipment. Buoyancy corrections are required in accurate work. Burets should be read in a reproducible manner and drained slowly for best results. Always interpolate between markings to obtain accuracy one decimal place beyond the graduations. Volumetric flasks are used to prepare solutions with known volume. Transfer pipets deliver fixed volumes; less accurate measuring pipets deliver variable volumes. Do not be lulled into complacency by the nice digital reading on a micropipet. Unless your pipet has been calibrated recently and your personal technique tested, micropipets can have gross errors. Filtration and collection of precipitates require careful technique, as does the drying of reagents, precipitates, and glassware in ovens and desiccators. Volumetric glassware is calibrated by weighing water contained in or delivered by the vessel. In the most careful work, solution concentrations and volumes of vessels should be corrected for changes in temperature.

If you plan to use spreadsheets in this course, you should know how to enter formulas in a spreadsheet and how to draw a graph of data in a spreadsheet.

Exercises

2-A. What is the true mass of water if the measured mass in the atmosphere is 5.397 4 g? When you look up the density of water, assume that the lab temperature is **(a)** 15°C and **(b)** 25°C. Take the density of air to be 0.001 2 g/mL and the density of balance weights to be 8.0 g/mL.

2-B. A sample of ferric oxide (Fe_2O_3, density = 5.24 g/mL) obtained from ignition of a gravimetric precipitate weighed 0.296 1 g in the atmosphere. What is the true mass in vacuum?

2-C. A solution of potassium permanganate ($KMnO_4$) was found by titration to be 0.051 38 M at 24°C. What was the molarity when the lab temperature dropped to 16°C?

2-D. Water was drained from a buret between the 0.12- and 15.78-mL marks. The apparent volume delivered was 15.78 − 0.12 = 15.66 mL. Measured in the air at 22°C, the mass of water delivered was 15.569 g. What was the true volume?

2-E. To familiarize yourself with your spreadsheet and graphing software, reproduce the spreadsheet in Figure 2-19 and the graph in Figure 2-21.

Problems

Safety and Lab Notebook

2-1. What is the primary safety rule and what is your implied responsibility to make it work?

2-2. After the safety features and procedures in your laboratory have been explained to you, make a list of them.

2-3. In Box 2-1, why is Pb^{2+} converted into $PbSiO_3$ before disposal in an approved landfill?

2-4. Explain what each of the three numbered hazard ratings means for 37 wt% HC1 in Figure 2-2.

2-5. State three essential attributes of a lab notebook.

Analytical Balance

2-6. Explain the principles of operation of electronic and mechanical balances.

2-7. Why is the buoyancy correction equal to 1 in Figure 2-5 when the density of the object being weighed is 8.0 g/mL?

2-8. Pentane (C_5H_{12}) is a liquid with a density of 0.626 g/mL near 25°C. Use Equation 2-1 to find the true mass of pentane when the mass weighed in air is 14.82 g. Assume that the air density is 0.001 2 g/mL and the balance weight density is 8.0 g/mL.

2-9. The densities (g/mL) of several substances are: acetic acid, 1.05; CCl_4, 1.59; sulfur, 2.07; lithium, 0.53; mercury, 13.5; PbO_2, 9.4; lead, 11.4; iridium, 22.5. From Figure 2-5, predict which substance will have the smallest percentage of buoyancy correction and which will have the greatest.

2-10. Potassium hydrogen phthalate is a primary standard used to measure the concentration of NaOH solutions. Find the true mass of potassium hydrogen phthalate (density = 1.636 g/mL) if the apparent mass weighed in air is 4.236 6 g. If you did not correct the mass for buoyancy, would the calculated molarity of NaOH be too high or too low? By what percentage?

2-11. **(a)** Use the ideal gas law (Problem 1-16) to calculate the density (g/mL) of helium at 20°C and 1.00 bar.
(b) Find the true mass of sodium metal (density = 0.97 g/mL) weighed in a glove box with a helium atmosphere, if the apparent mass was 0.823 g and the balance weight density is 8.0 g/mL.

2-12. **(a)** What is the vapor pressure of water in the air at 20°C if the relative humidity is 42%? The vapor pressure of water at 20°C at equilibrium is 2 330 Pa. (*Relative humidity* is the percentage of the equilibrium water vapor pressure in the air.)
(b) Use note 11 for Chapter 2 at the end of the book to find the air density (g/mL, not g/L) under the conditions of part **(a)** if the barometric pressure is 94.0 kPa.
(c) What is the true mass of water in part **(b)** if the balance indicates that 1.000 0 g is present (balance weight density = 8.0 g/mL)?

2-13. *Effect of altitude on electronic balance.* If an object weighs m_a grams at distance r_a from the center of the earth, it will weigh $m_b = m_a(r_a^2/r_b^2)$ when raised to r_b. An object weighs 100.000 0 g on the 1st floor of a building at r_a = 6 370 km. How much will it weigh on the 10th floor, which is 30 m higher?

Glassware and Thermal Expansion

2-14. What do the symbols "TD" and "TC" mean on volumetric glassware?

2-15. Describe how to prepare 250.0 mL of 0.150 0 M K_2SO_4 with a volumetric flask.

2-16. When is it preferable to use a plastic volumetric flask instead of a more accurate glass flask?

17. Describe how to deliver 5.00 mL of liquid by using a transfer pet.

18. Which is more accurate, a transfer pipet or a measuring pipet?

19. What is the purpose of the trap in Figure 2-14 and the watch-lass in Figure 2-17?

20. Which drying agent is more efficient, Drierite or phosphorus entoxide?

21. An empty 10-mL volumetric flask weighs 10.263 4 g. When he flask is filled to the mark with distilled water and weighed again n the air at 20°C, the mass is 20.214 4 g. What is the true volume of the flask at 20°C?

22. By what percentage does a dilute aqueous solution expand when heated from 15° to 25°C? If a 0.500 0 M solution is prepared at 15°C, what would its molarity be at 25°C?

23. The true volume of a 50-mL volumetric flask is 50.037 mL at 20°C. What mass of water measured **(a)** in vacuum and **(b)** in air at 20°C would be contained in the flask?

24. You want to prepare 500.0 mL of 1.000 M KNO_3 at 20°C, but the lab (and water) temperature is 24°C at the time of preparation. How many grams of solid KNO_3 (density = 2.109 g/mL) should be dissolved in a volume of 500.0 mL at 24°C to give a concentration of 1.000 M at 20°C? What apparent mass of KNO_3 weighed in air is required?

25. Glass is a notorious source of metal ion contamination. Three glass bottles were crushed and sieved to collect 1-mm pieces.[20] To see how much Al^{3+} could be extracted, 200 mL of a 0.05 M solution of the metal-binding compound EDTA was stirred with 0.50 g of ~1-mm glass particles in a polyethylene flask. The Al content of the solution after 2 months was 5.2 μM. The total Al content of the glass, measured after completely dissolving some glass in 48 wt% HF with microwave heating, was 0.80 wt%. What fraction of the Al was extracted from glass by EDTA?

26. The efficiency of a gas chromatography column is measured by a parameter called plate height (H, mm), which is related to the gas flow rate (u, mL/min) by the van Deemter equation: $H = A + B/u + Cu$, where A, B, and C are constants. Prepare a spreadsheet with a graph showing values of H as a function of u for u = 4, 6, 8, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mL/min. Use the values A = 1.65 mm, B = 25.8 mm · mL/min, and C = 0.023 6 mm · min/mL.

Reference Procedure: Calibrating a 50-mL Buret

This procedure tells how to construct a graph such as Figure 3-3 to convert the measured volume delivered by a buret to the true volume delivered at 20°C.

1. Fill the buret with distilled water and force any air bubbles out the tip. See whether the buret drains without leaving drops on the walls. If drops are left, clean the buret with soap and water or soak it with cleaning solution.[13] Adjust the meniscus to be at or slightly below 0.00 mL, and touch the buret tip to a beaker to remove the suspended drop of water. Allow the buret to stand for 5 min while you weigh a 125-mL flask fitted with a rubber stopper. (Hold the flask with a tissue or paper towel, not with your hands, to prevent fingerprint residue from changing its mass.) If the level of the liquid in the buret has changed, tighten the stopcock and repeat the procedure. Record the level of the liquid.
2. Drain approximately 10 mL of water at a rate < 20 mL/min into the weighed flask, and cap it tightly to prevent evaporation. Allow about 30 s for the film of liquid on the walls to descend before you read the buret. Estimate all readings to the nearest 0.01 mL. Weigh the flask again to determine the mass of water delivered.
3. Now drain the buret from 10 to 20 mL, and measure the mass of water delivered. Repeat the procedure for 30, 40, and 50 mL. Then do the entire procedure (10, 20, 30, 40, 50 mL) a second time.
4. Use Table 2-7 to convert the mass of water into the volume delivered. Repeat any set of duplicate buret corrections that do not agree to within 0.04 mL. Prepare a calibration graph like that in Figure 3-3, showing the correction factor at each 10-mL interval.

Example Buret Calibration

When draining the buret at 24°C, you observe the following values:

Final reading	10.01	10.08 mL
Initial reading	0.03	0.04
Difference	9.98	10.04 mL
Mass	9.984	10.056 g
Actual volume delivered	10.02	10.09 mL
Correction	+0.04	+0.05 mL
Average correction	+0.045 mL	

To calculate the actual volume delivered when 9.984 g of water is delivered at 24°C, look at the column of Table 2-7 headed "Corrected to 20°C." In the row for 24°C, you find that 1.000 0 g of water occupies 1.003 8 mL. Therefore, 9.984 g occupies (9.984 g)(1.003 8 mL/g) = 10.02 mL. The average correction for both sets of data is +0.045 mL.

To obtain the correction for a volume greater than 10 mL, add successive masses of water collected in the flask. Suppose that the following masses were measured:

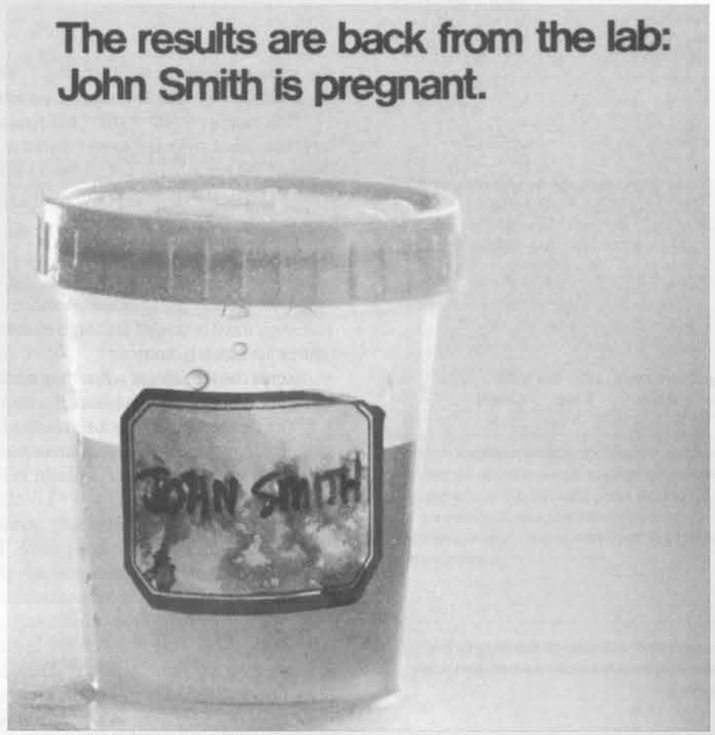
Volume interval (mL)	Mass delivered (g)
0.03–10.01	9.984
10.01–19.90	9.835
19.90–30.06	10.071
Sum 30.03 mL	29.890 g

The total volume of water delivered is (29.890 g)(1.003 8 mL/g) = 30.00 mL. Because the indicated volume is 30.03 mL, the buret correction at 30 mL is −0.03 mL.

What does this mean? Suppose that Figure 3-3 applies to your buret. If you begin a titration at 0.04 mL and end at 29.00 mL, you would deliver 28.96 mL if the buret were perfect. Figure 3-3 tells you that the buret delivers 0.03 mL less than the indicated amount, so only 28.93 mL were actually delivered. To use the calibration curve, either begin all titrations near 0.00 mL or correct both the initial and the final readings. Use the calibration curve whenever you use your buret.

3 Experimental Error

EXPERIMENTAL ERROR



[Courtesy 3M Company, St. Paul, MN.]

Some laboratory errors are more obvious than others, but there is error associated with every measurement. There is no way to measure the "true value" of anything. The best we can do in a chemical analysis is to carefully apply a technique that experience tells us is reliable. Repetition of one method of measurement several times tells us the *precision* (reproducibility) of the measurement. If the results of measuring the same quantity by different methods agree with one another, then we become confident that the results are *accurate*, which means they are near the "true" value.

Suppose that you determine the density of a mineral by measuring its mass (4.635 ± 0.002 g) and volume (1.13 ± 0.05 mL). Density is mass per unit volume: 4.635 g/1.13 mL = 4.101 8 g/mL. The uncertainties in measured mass and volume are ±0.002 g and ±0.05 mL, but what is the uncertainty in the computed density? And how many significant figures should be used for the density? This chapter discusses the propagation of uncertainty in lab calculations.

3-1 Significant Figures

Significant figures: minimum number of digits required to express a value in scientific notation without loss of accuracy

The number of **significant figures** is the minimum number of digits needed to write a given value in scientific notation without loss of accuracy. The number 142.7 has four significant figures, because it can be written 1.427×10^2. If you write $1.427\,0 \times 10^2$, you imply that

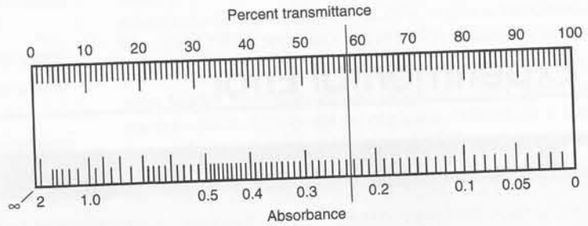


Figure 3-1 Scale of a Bausch and Lomb Spectronic 20 spectrophotometer. Percent transmittance is a linear scale and absorbance is a logarithmic scale.

you know the value of the digit after 7, which is not the case for the number 142.7. The number $1.427\,0 \times 10^2$ has five significant figures.

The number 6.302×10^{-6} has four significant figures, because all four digits are necessary. You could write the same number as 0.000 006 302, which also has just *four* significant figures. The zeros to the left of the 6 are merely holding decimal places. The number 92 500 is ambiguous. It could mean any of the following:

9.25×10^4	3 significant figures
9.250×10^4	4 significant figures
$9.250\,0 \times 10^4$	5 significant figures

You should write one of the three numbers above, instead of 92 500, to indicate how many figures are actually known.

Significant zeros below are **bold**:
106 0.010 6 0.106 0.106 0

Zeros are significant when they occur (1) in the middle of a number or (2) at the end of a number on the right-hand side of a decimal point.

The last significant digit (farthest to the right) in a measured quantity always has some associated uncertainty. The minimum uncertainty is ± 1 in the last digit. The scale of a Spectronic 20 spectrophotometer is drawn in Figure 3-1. The needle in the figure appears to be at an absorbance value of 0.234. We say that this number has three significant figures because the numbers 2 and 3 are completely certain and the number 4 is an estimate. The value might be read 0.233 or 0.235 by other people. The percent transmittance is near 58.3. Because the transmittance scale is smaller than the absorbance scale at this point, there is more uncertainty in the last digit of transmittance. A reasonable estimate of uncertainty might be 58.3 ± 0.2. There are three significant figures in the number 58.3.

Interpolation: Estimate all readings to the nearest tenth of the distance between scale divisions.

When reading the scale of any apparatus, try to estimate to the nearest tenth of a division. On a 50-mL buret, which is graduated to 0.1 mL, read the level to the nearest 0.01 mL. For a ruler calibrated in millimeters, estimate distances to the nearest 0.1 mm.

There is uncertainty in any *measured* quantity, even if the measuring instrument has a digital readout that does not fluctuate. When a digital pH meter indicates a pH of 3.51, there is uncertainty in the digit 1 (and maybe even in the digit 5). By contrast, some numbers are exact—with an infinite number of unwritten significant digits. To calculate the average height of four people, you would divide the sum of heights (which is a measured quantity with some uncertainty) by the integer 4. There are exactly 4 people, not 4.000 ± 0.002 people!

3-2 Significant Figures in Arithmetic

We now consider how many digits to retain in the answer after you have performed arithmetic operations with your data. Rounding should only be done on the *final answer* (not intermediate results), to avoid accumulating round-off errors.

Addition and Subtraction

If the numbers to be added or subtracted have equal numbers of digits, the answer goes to the *same decimal place* as in any of the individual numbers:

$$\begin{array}{r} 1.362 \times 10^{-4} \\ +\ 3.111 \times 10^{-4} \\ \hline 4.473 \times 10^{-4} \end{array}$$

The number of significant figures in the answer may exceed or be less than that in the original data.

$$\begin{array}{r} 5.345 \\ +\ 6.728 \\ \hline 12.073 \end{array} \qquad \begin{array}{r} 7.26 \times 10^{14} \\ -\ 6.69 \times 10^{14} \\ \hline 0.57 \times 10^{14} \end{array}$$

If the numbers being added do not have the same number of significant figures, we are limited by the least-certain one. For example, the molecular mass of KrF_2 is known only to the third decimal place, because we only know the atomic mass of Kr to three decimal places:

$$\begin{array}{rl} 18.998\,403\,2 & \text{(F)} \\ +\ 18.998\,403\,2 & \text{(F)} \\ +\ 83.798 & \text{(Kr)} \\ \hline 121.794\,806\,4 & \end{array}$$

Not significant

The number 121.794 806 4 should be rounded to 121.795 as the final answer.

Inspect the legend of the periodic table inside the cover of this book. Be sure you can interpret uncertainties in atomic masses. For F and Kr, the atomic masses are

F: $18.998\,403\,2 \pm 0.000\,000\,5$
Kr: 83.798 ± 0.002

Rules for rounding off numbers

When rounding off, look at *all* the digits *beyond* the last place desired. In the preceding example, the digits 806 4 lie beyond the last significant decimal place. Because this number is more than halfway to the next higher digit, we round the 4 up to 5 (that is, we round up to 121.795 instead of down to 121.794). If the insignificant figures were less than halfway, we would round down. For example, 121.794 3 is rounded to 121.794.

In the special case where the number is exactly halfway, round to the nearest *even* digit. Thus, 43.55 is rounded to 43.6, if we can only have three significant figures. If we are retaining only three figures, 1.425×10^{-9} becomes 1.42×10^{-9}. The number $1.425\,01 \times 10^{-9}$ would become 1.43×10^{-9}, because 501 is more than halfway to the next digit. The rationale for rounding to an even digit is to avoid systematically increasing or decreasing results through successive round-off errors. Half the round-offs will be up and half down.

In the addition or subtraction of numbers expressed in scientific notation, all numbers should first be expressed with the same exponent:

Addition and subtraction: Express all numbers with the same exponent and align all numbers with respect to the decimal point. Round off the answer according to the number of decimal places in the number with the fewest decimal places.

$$\begin{array}{r} 1.632 \times 10^5 \\ +\ 4.107 \times 10^3 \\ +\ 0.984 \times 10^6 \end{array} \rightarrow \begin{array}{rl} 1.632 & \times 10^5 \\ +\ 0.041\,07 & \times 10^5 \\ +\ 9.84 & \times 10^5 \\ \hline 11.51 & \times 10^5 \end{array}$$

The sum $11.513\,07 \times 10^5$ is rounded to 11.51×10^5 because the number 9.84×10^5 limits us to two decimal places when all numbers are expressed as multiples of 10^5.

Multiplication and Division

In multiplication and division, we are normally limited to the number of digits contained in the number with the fewest significant figures:

$$\begin{array}{r} 3.26 \times 10^{-5} \\ \times\ 1.78 \\ \hline 5.80 \times 10^{-5} \end{array} \qquad \begin{array}{rl} 4.317\,9 & \times 10^{12} \\ \times\ 3.6 & \times 10^{-19} \\ \hline 1.6 & \times 10^{-6} \end{array} \qquad \begin{array}{r} 34.60 \\ \div\ 2.462\,87 \\ \hline 14.05 \end{array}$$

The power of 10 has no influence on the number of figures that should be retained.

Logarithms and Antilogarithms

The base 10 **logarithm** of n is the number a, whose value is such that $n = 10^a$:

Logarithm of n: $\quad n = 10^a$ means that $\log n = a$ **(3-1)**

For example, 2 is the logarithm of 100 because $100 = 10^2$. The logarithm of 0.001 is -3 because $0.001 = 10^{-3}$. To find the logarithm of a number with your calculator, enter the number and press the *log* function.

$10^{-3} = \frac{1}{10^3} = \frac{1}{1\,000} = 0.001$

In Equation 3-1, the number n is said to be the **antilogarithm** of a. That is, the antilogarithm of 2 is 100 because $10^2 = 100$, and the antilogarithm of -3 is 0.001 because $10^{-3} = 0.001$. Your calculator has either a 10^x key or an *antilog* key. To find the antilogarithm of a number, enter it in your calculator and press 10^x (or *antilog*).

Number of digits in ***mantissa*** of log x = number of significant figures in x:

$$\log(\underbrace{5.403 \times 10^{-8}}_{4\text{ digits}}) = -\underbrace{7.267\,4}_{4\text{ digits}}$$

A logarithm is composed of a **characteristic** and a **mantissa.** The characteristic is the integer part and the mantissa is the decimal part:

$$\log 339 = \underbrace{2.530}_{\substack{\text{Characteristic}\\=2}\quad\text{Mantissa}=0.530} \qquad \log 3.39 \times 10^{-5} = \underbrace{-4.470}_{\substack{\text{Characteristic}\\=-4}\quad\text{Mantissa}=0.470}$$

The number 339 can be written 3.39×10^2. *The number of digits in the mantissa of log 339 should equal the number of significant figures in 339.* The logarithm of 339 is properly expressed as 2.530. The *characteristic,* 2, corresponds to the exponent in 3.39×10^2.

To see that the third decimal place is the last significant place, consider the following results:

$$10^{2.531} = 340\ (339.6)$$
$$10^{2.530} = 339\ (338.8)$$
$$10^{2.529} = 338\ (338.1)$$

The numbers in parentheses are the results prior to rounding to three figures. Changing the exponent in the third decimal place changes the answer in the third place of 339.

In the conversion of a logarithm into its antilogarithm, *the number of significant figures in the antilogarithm should equal the number of digits in the mantissa.* Thus,

Number of digits in antilog x ($=10^x$) = number of significant figures in ***mantissa*** of x:

$$\text{antilog}\,(\underbrace{-3.42}_{2\text{ digits}}) = 10^{\underbrace{-3.42}_{2\text{ digits}}} = \underbrace{3.8}_{2\text{ digits}} \times 10^{-4}$$

$$10^{\underbrace{6.142}_{3\text{ digits}}} = \underbrace{1.39}_{3\text{ digits}} \times 10^6$$

Here are several examples showing the proper use of significant figures:

$$\log 0.001\,237 = -2.907\,6 \qquad \text{antilog}\,4.37 = 2.3 \times 10^4$$
$$\log 1\,237 = 3.092\,4 \qquad 10^{4.37} = 2.3 \times 10^4$$
$$\log 3.2 = 0.51 \qquad 10^{-2.600} = 2.51 \times 10^{-3}$$

Significant Figures and Graphs

Problem 3-8 shows you how to control gridlines in an Excel graph.

When drawing a graph on a computer, consider whether the graph is meant to display qualitative behavior of the data (Figure 3-2) or precise values. If someone will use the graph (such as Figure 3-3) to read points, it should at least have tic marks on both sides of the horizontal and vertical scales. Better still is a fine grid superimposed on the graph.

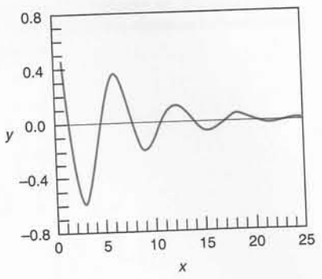


Figure 3-2 Example of a graph intended to show the qualitative behavior of the function $y = e^{-x/6} \cos x$. You are not expected to be able to read coordinates accurately on this graph.

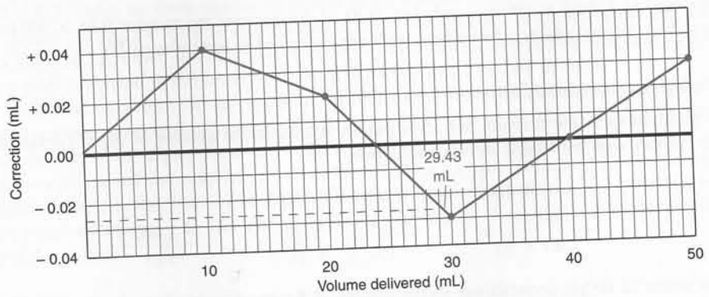


Figure 3-3 Calibration curve for a 50-mL buret. The volume delivered can be read to the nearest 0.1 mL. If your buret reading is 29.43 mL, you can find the correction factor accurately enough by locating 29.4 mL on the graph. The correction factor on the ordinate (y-axis) for 29.4 mL on the abscissa (x-axis) is −0.03 mL (to the nearest 0.01 mL).

3-3 Types of Error

Every measurement has some uncertainty, which is called *experimental error.* Conclusions can be expressed with a high or a low degree of confidence, but never with complete certainty. Experimental error is classified as either *systematic* or *random.*

Systematic Error

Systematic error is a consistent error that can be detected and corrected. Box 3-1 describes Standard Reference Materials designed to reduce systematic errors.

Systematic error, also called **determinate error,** arises from a flaw in equipment or the design of an experiment. If you conduct the experiment again in exactly the same manner, the error is reproducible. In principle, systematic error can be discovered and corrected, although this may not be easy.

For example, a pH meter that has been standardized incorrectly produces a systematic error. Suppose you think that the pH of the buffer used to standardize the meter is 7.00, but it is really 7.08. Then all your pH readings will be 0.08 pH unit too low. When you read a pH of 5.60, the actual pH of the sample is 5.68. This systematic error could be discovered by using a second buffer of known pH to test the meter.

Another systematic error arises from an uncalibrated buret. The manufacturer's tolerance for a Class A 50-mL buret is ±0.05 mL. When you think you have delivered 29.43 mL, the real volume could be anywhere from 29.38 to 29.48 mL and still be within tolerance. One way to correct for an error of this type is to construct a calibration curve, such as that in Figure 3-3, by the procedure on page 38. To do this, deliver distilled water from the buret into a flask and weigh it. Determine the volume of water from its mass by using Table 2-7. Figure 3-3 tells us to apply a correction factor of −0.03 mL to the measured value of 29.43 mL. The actual volume delivered is 29.43 − 0.03 = 29.40 mL.

A key feature of systematic error is that it is reproducible. For the buret just discussed, the error is always −0.03 mL when the buret reading is 29.43 mL. Systematic error may always be positive in some regions and always negative in others. With care and cleverness, you can detect and correct a systematic error.

Ways to detect systematic error:
1. Analyze a known sample, such as a Standard Reference Material. Your method should reproduce the known answer. (See Box 15-1 for an example.)
2. Analyze "blank" samples containing none of the analyte being sought. If you observe a nonzero result, your method responds to more than you intend. Section 5-1 discusses different kinds of blanks.
3. Use different analytical methods to measure the same quantity. If results do not agree, there is error in one (or more) of the methods.
4. *Round robin* experiment: Different people in several laboratories analyze identical samples by the same or different methods. Disagreement beyond the estimated random error is systematic error.

Random Error

Random error cannot be eliminated, but it might be reduced by a better experiment.

Random error, also called **indeterminate error,** arises from the effects of uncontrolled (and maybe uncontrollable) variables in the measurement. Random error has an equal chance of being positive or negative. It is always present and cannot be corrected. There is random error associated with reading a scale. Different people reading the scale in Figure 3-1 report a range of values representing their subjective interpolation between the markings. One person reading the same instrument several times might report several different readings. Another random error results from electrical noise in an instrument. Positive and negative fluctuations occur with approximately equal frequency and cannot be completely eliminated.

Precision and Accuracy

Precision: reproducibility
Accuracy: nearness to the "truth"

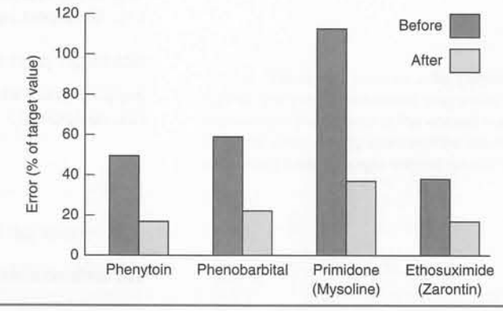
Precision describes the reproducibility of a result. If you measure a quantity several times and the values agree closely with one another, your measurement is precise. If the values vary widely, your measurement is not precise. **Accuracy** describes how close a measured value is to the "true" value. If a known standard is available (such as a Standard Reference Material described in Box 3-1), accuracy is how close your value is to the known value.

Box 3-1 Standard Reference Materials

Inaccurate laboratory measurements can mean wrong medical diagnosis and treatment, lost production time, wasted energy and materials, manufacturing rejects, and product liability. The U.S. National Institute of Standards and Technology and national standards laboratories around the world distribute Standard Reference Materials, such as metals, chemicals, rubber, plastics, engineering materials, radioactive substances, and environmental and clinical standards that can be used to test the accuracy of analytical procedures.[1]

For example, in treating patients with epilepsy, physicians depend on laboratory tests to measure concentrations of anticonvulsant drugs in blood serum. Drug levels that are too low lead to seizures; high levels are toxic. Because tests of identical serum specimens at different laboratories were giving an unacceptably wide range of results, the National Institute of Standards and Technology developed a Standard Reference Material containing known levels of antiepilepsy drugs in serum. The reference material now enables different laboratories to detect and correct errors in their assay procedures.

Before the introduction of this reference material, five laboratories analyzing identical samples reported a range of results with relative errors of 40% to 110% of the expected value. After distribution of the reference material, the error was reduced to 20% to 40%.



A measurement might be reproducible, but wrong. If you made a mistake preparing a solution for a titration, you might do a series of reproducible titrations but report an incorrect result because the concentration of the titrating solution was not what you intended. In this case, the precision is good but the accuracy is poor. Conversely, it is possible to make poorly reproducible measurements clustered around the correct value. In this case, the precision is poor but the accuracy is good. An ideal procedure is both precise and accurate.

Accuracy is defined as nearness to the "true" value. The word *true* is in quotes because somebody must *measure* the "true" value, and there is error associated with *every* measurement. The "true" value is best obtained by an experienced person using a well-tested procedure. It is desirable to test the result by using different procedures, because, even though each method might be precise, systematic error could lead to poor agreement between methods. Good agreement among several methods affords us confidence, but never proof, that results are accurate.

Absolute and Relative Uncertainty

An uncertainty of ±0.02 means that, when the reading is 13.33, the true value could be anywhere in the range 13.31 to 13.35.

Absolute uncertainty expresses the margin of uncertainty associated with a measurement. If the estimated uncertainty in reading a calibrated buret is ±0.02 mL, we say that ±0.02 mL is the absolute uncertainty associated with the reading.

Relative uncertainty compares the size of the absolute uncertainty with the size of its associated measurement. The relative uncertainty of a buret reading of 12.35 ± 0.02 mL is a dimensionless quotient:

Relative uncertainty:

$$\text{Relative uncertainty} = \frac{\text{absolute uncertainty}}{\text{magnitude of measurement}} \tag{3-2}$$

$$= \frac{0.02 \text{ mL}}{12.35 \text{ mL}} = 0.002$$

If you use a 50-mL buret, design your titration to require 20–40 mL of reagent to produce a small relative uncertainty of 0.1–0.05%.

In a gravimetric analysis, plan to have enough precipitate for a low relative uncertainty. If weighing precision is ±0.3 mg, a 100-mg precipitate has a relative weighing error of 0.3% and a 300-mg precipitate has an uncertainty of 0.1%.

The percent relative uncertainty is simply

Percent relative uncertainty:

$$\text{Percent relative uncertainty} = 100 \times \text{relative uncertainty} \tag{3-3}$$

$$= 100 \times 0.002 = 0.2\%$$

If the absolute uncertainty in reading a buret is constant at ±0.02 mL, the percent relative uncertainty is 0.2% for a volume of 10 mL and 0.1% for a volume of 20 mL.

3-4 Propagation of Uncertainty from Random Error

We can usually estimate or measure the random error associated with a measurement, such as the length of an object or the temperature of a solution. The uncertainty might be based on how well we can read an instrument or on our experience with a particular method. If possible, uncertainty is expressed as the *standard deviation* or as a *confidence interval,* which are discussed in Chapter 4. This section applies only to random error. We assume that systematic error has been detected and corrected.

By far, most propagation of uncertainty computations that you will encounter deal with random error, not systematic error. Our goal is always to eliminate systematic error.

For most experiments, we need to perform arithmetic operations on several numbers, each of which has a random error. The most likely uncertainty in the result is not simply the sum of the individual errors, because some of them are likely to be positive and some negative. We expect some cancellation of errors.

Addition and Subtraction

Suppose you wish to perform the following arithmetic, in which the experimental uncertainties, designated e_1, e_2, and e_3, are given in parentheses.

$$\begin{array}{l} 1.76\ (\pm 0.03) \leftarrow e_1 \\ +\ 1.89\ (\pm 0.02) \leftarrow e_2 \\ \underline{-\ 0.59\ (\pm 0.02) \leftarrow e_3} \\ 3.06\ (\pm e_4) \end{array} \tag{3-4}$$

The arithmetic answer is 3.06. But what is the uncertainty associated with this result?

For addition and subtraction, the uncertainty in the answer is obtained from the *absolute uncertainties* of the individual terms as follows:

Uncertainty in addition and subtraction:

$$e_4 = \sqrt{e_1^2 + e_2^2 + e_3^2} \tag{3-5}$$

For addition and subtraction, use *absolute* uncertainty.

For the sum in Equation 3-4, we can write

$$e_4 = \sqrt{(0.03)^2 + (0.02)^2 + (0.02)^2} = 0.04_1$$

The absolute uncertainty e_4 is ±0.04, and we express the answer as 3.06 ± 0.04. Although there is only one significant figure in the uncertainty, we wrote it initially as 0.04_1, with the first insignificant figure subscripted. We retain one or more insignificant figures to avoid introducing round-off errors into later calculations through the number 0.04_1. The insignificant figure was subscripted to remind us where the last significant figure should be at the conclusion of the calculations.

To find the percent relative uncertainty in the sum of Equation 3-4, we write

$$\text{Percent relative uncertainty} = \frac{0.04_1}{3.06} \times 100 = 1._3\%$$

The uncertainty, 0.04_1, is $1._3\%$ of the result, 3.06. The subscript 3 in $1._3\%$ is not significant. It is sensible to drop the insignificant figures now and express the final result as

3.06 (±0.04) (absolute uncertainty)
3.06 (±1%) (relative uncertainty)

For addition and subtraction, use absolute uncertainty. Relative uncertainty can be found at the end of the calculation.

Example Uncertainty in a Buret Reading

The volume delivered by a buret is the difference between final and initial readings. If the uncertainty in each reading is ±0.02 mL, what is the uncertainty in the volume delivered?

Solution Suppose that the initial reading is 0.05 (±0.02) mL and the final reading is 17.88 (±0.02) mL. The volume delivered is the difference:

$$\begin{array}{l} 17.88\ (\pm 0.02) \\ \underline{-\ 0.05\ (\pm 0.02)} \\ 17.83\ (\pm e) \end{array} \qquad e = \sqrt{0.02^2 + 0.02^2} = 0.02_8 \approx 0.03$$

Regardless of the initial and final readings, if the uncertainty in each one is ±0.02 mL, the uncertainty in volume delivered is ±0.03 mL.

Multiplication and Division

For multiplication and division, first convert all uncertainties into percent relative uncertainties. Then calculate the error of the product or quotient as follows:

Uncertainty in multiplication and division:

$$\%e_4 = \sqrt{(\%e_1)^2 + (\%e_2)^2 + (\%e_3)^2} \tag{3-6}$$

For multiplication and division, use percent relative uncertainty.

For example, consider the following operations:

$$\frac{1.76\ (\pm 0.03) \times 1.89\ (\pm 0.02)}{0.59\ (\pm 0.02)} = 5.64 \pm e_4$$

First convert absolute uncertainties into percent relative uncertainties.

$$\frac{1.76\ (\pm 1._7\%) \times 1.89\ (\pm 1._1\%)}{0.59\ (\pm 3._4\%)} = 5.64 \pm e_4$$

Advice Retain one or more extra insignificant figures until you have finished your entire calculation. Then round to the correct number of digits. When storing intermediate results in a calculator, keep all digits without rounding.

Then find the percent relative uncertainty of the answer by using Equation 3-6.

$$\%e_4 = \sqrt{(1._7)^2 + (1._1)^2 + (3._4)^2} = 4._0\%$$

The answer is 5.6_4 ($\pm 4._0\%$).

To convert relative uncertainty into absolute uncertainty, find $4._0\%$ of the answer.

$$4._0\% \times 5.6_4 = 0.04_0 \times 5.6_4 = 0.2_3$$

For multiplication and division, use percent relative uncertainty. Absolute uncertainty can be found at the end of the calculation.

The answer is 5.6_4 ($\pm 0.2_3$). Finally, drop the insignificant digits.

$$5.6\ (\pm 0.2) \qquad \text{(absolute uncertainty)}$$
$$5.6\ (\pm 4\%) \qquad \text{(relative uncertainty)}$$

The denominator of the original problem, 0.59, limits the answer to two digits.

Mixed Operations

Now consider a computation containing subtraction and division:

$$\frac{[1.76\ (\pm 0.03) - 0.59\ (\pm 0.02)]}{1.89\ (\pm 0.02)} = 0.619_0 \pm ?$$

First work out the difference in the numerator, using absolute uncertainties. Thus,

$$1.76\ (\pm 0.03) - 0.59\ (\pm 0.02) = 1.17\ (\pm 0.03_6)$$

because $\sqrt{(0.03)^2 + (0.02)^2} = 0.03_6$.

Then convert into percent relative uncertainties. Thus,

$$\frac{1.17\ (\pm 0.03_6)}{1.89\ (\pm 0.02)} = \frac{1.17\ (\pm 3._1\%)}{1.89\ (\pm 1._1\%)} = 0.619_0\ (\pm 3._3\%)$$

because $\sqrt{(3._1\%)^2 + (1._1\%)^2} = 3._3\%$.

The percent relative uncertainty is $3._3\%$, so the absolute uncertainty is $0.03_3 \times 0.619_0 = 0.02_0$. The final answer can be written as

$$0.619\ (\pm 0.02_0) \qquad \text{(absolute uncertainty)}$$
$$0.619\ (\pm 3._3\%) \qquad \text{(relative uncertainty)}$$

The result of a calculation ought to be written in a manner consistent with its uncertainty.

Because the uncertainty begins in the 0.01 decimal place, it is reasonable to round the result to the 0.01 decimal place:

$$0.62\ (\pm 0.02) \qquad \text{(absolute uncertainty)}$$
$$0.62\ (\pm 3\%) \qquad \text{(relative uncertainty)}$$

The *Real* Rule for Significant Figures

The real rule: The first uncertain figure is the last significant figure.

The first digit of the absolute uncertainty is the last significant digit in the answer. For example, in the quotient

$$\frac{0.002\ 364\ (\pm 0.000\ 003)}{0.025\ 00(\pm 0.000\ 05)} = 0.094\ 6\ (\pm 0.000\ 2)$$

the uncertainty ($\pm 0.000\ 2$) occurs in the fourth decimal place. Therefore, the answer 0.094 6 is properly expressed with *three* significant figures, even though the original data have four figures. The first uncertain figure of the answer is the last significant figure. The quotient

$$\frac{0.002\ 664\ (\pm 0.000\ 003)}{0.025\ 00\ (\pm 0.000\ 05)} = 0.106\ 6\ (\pm 0.000\ 2)$$

is expressed with *four* significant figures because the uncertainty occurs in the fourth place. The quotient

$$\frac{0.821\ (\pm 0.002)}{0.803\ (\pm 0.002)} = 1.022\ (\pm 0.004)$$

is expressed with *four* figures even though the dividend and divisor each have *three* figures.

It is all right to keep one extra digit when an answer lies between 1 and 2.

Now you can appreciate why *it is all right to keep one extra digit when an answer lies between 1 and 2*. The quotient 82/80 is better written as 1.02 than 1.0. If I write 1.0, you can surmise that the uncertainty is at least $1.0 \pm 0.1 = \pm 10\%$. The actual uncertainty lies in the second decimal place, not the first decimal place.

Example Significant Figures in Laboratory Work

You prepared a 0.250 M NH_3 solution by diluting 8.45 (± 0.04) mL of 28.0 (± 0.5) wt% NH_3 [density = 0.899 (± 0.003) g/mL] up to 500.0 (± 0.2) mL. Find the uncertainty in 0.250 M. The molecular mass of NH_3, 17.030 5 g/mol, has negligible uncertainty relative to other uncertainties in this problem.

Solution To find the uncertainty in molarity, we need to find the uncertainty in moles delivered to the 500-mL flask. The concentrated reagent contains 0.899 (± 0.003) g of solution per milliliter. Weight percent tells us that the reagent contains 0.280 (± 0.005) g of NH_3 per gram of solution. In our calculations, we retain extra insignificant digits and round off only at the end.

$$\text{Grams of } NH_3 \text{ per mL in concentrated reagent} = 0.899\ (\pm 0.003)\ \frac{\text{g solution}}{\text{mL}} \times 0.280\ (\pm 0.005)\ \frac{\text{g } NH_3}{\text{g solution}}$$
$$= 0.899\ (\pm 0.334\%)\ \frac{\text{g solution}}{\text{mL}} \times 0.280\ (\pm 1.79\%)\ \frac{\text{g } NH_3}{\text{g solution}}$$
$$= 0.251\ 7\ (\pm 1.82\%)\ \frac{\text{g } NH_3}{\text{mL}}$$

because $\sqrt{(0.334\%)^2 + (1.79\%)^2} = 1.82\%$.

The rationale for finding the uncertainty in the molecular mass of NH_3 is explained in Section 3-5:

$$\begin{array}{ll} \text{N:} & 14.006\ 7 \pm 0.000\ 2 \\ +3\text{H:} & +3(1.007\ 94 \pm 0.000\ 07) \end{array}$$

$$\begin{array}{ll} \text{N:} & 14.006\ 7 \pm 0.000\ 2 \\ +3\text{H:} & +3.023\ 82 \pm 0.000\ 21 \\ \hline NH_3\text{:} & 17.030\ 52 \pm \sqrt{0.000\ 2^2 + 0.000\ 21^2} \\ = & 17.030\ 5_2 \pm 0.000\ 2_9 \\ = & 17.030\ 5 \pm 0.000\ 3 \end{array}$$

Next, we find the moles of ammonia contained in 8.45 (± 0.04) mL of concentrated reagent. The relative uncertainty in volume is 0.04/8.45 = 0.473%.

Convert absolute uncertainty into percent relative uncertainty for multiplication.

$$\text{mol } NH_3 = \frac{0.251\ 7\ (\pm 1.82\%)\ \frac{\text{g } NH_3}{\text{mL}} \times 8.45\ (\pm 0.473\%)\ \text{mL}}{17.030\ 5\ (\pm 0\%)\ \frac{\text{g } NH_3}{\text{mol}}}$$
$$= 0.124\ 9\ (\pm 1.88\%)\ \text{mol}$$

because $\sqrt{(1.82\%)^2 + (0.473\%)^2 + (0\%)^2} = 1.88\%$.

This much ammonia was diluted to 0.500 0 ($\pm 0.000\ 2$) L. The relative uncertainty in the final volume is 0.000 2/0.500 0 = 0.04%. The molarity is

$$\frac{\text{mol } NH_3}{\text{L}} = \frac{0.124\ 9\ (\pm 1.88\%)\ \text{mol}}{0.500\ 0\ (\pm 0.04\%)\ \text{L}}$$
$$= 0.249\ 8\ (\pm 1.88\%)\ \text{M}$$

because $\sqrt{(1.88\%)^2 + (0.04\%)^2} = 1.88\%$. The absolute uncertainty is 1.88% of 0.249 8 M = 0.004 7 M. The uncertainty in molarity is in the third decimal place, so our final, rounded answer is

$$[NH_3] = 0.250\ (\pm 0.005)\ \text{M}$$

Exponents and Logarithms

For the function $y = x^a$, the percent relative uncertainty in y ($\%e_y$) is equal to a times the percent relative uncertainty in x ($\%e_x$):

To calculate a power or root on your calculator, use the y^x button. For example, to find a cube root ($y^{1/3}$), raise y to the 0.333 333 333 . . . power with the y^x button.

Uncertainty for powers and roots:

$$y = x^a \quad \Rightarrow \quad \%e_y = a(\%e_x) \tag{3-7}$$

For example, if $y = \sqrt{x} = x^{1/2}$, a 2% uncertainty in x will yield a $(\frac{1}{2})(2\%) = 1\%$ uncertainty in y. If $y = x^2$, a 3% uncertainty in x leads to a (2)(3%) = 6% uncertainty in y (Box 3-2).

If y is the base 10 logarithm of x, then the absolute uncertainty in y (e_y) is proportional to the relative uncertainty in x, which is e_x/x:

Uncertainty for logarithm:

$$y = \log x \quad \Rightarrow \quad e_y = \frac{1}{\ln 10}\frac{e_x}{x} \approx 0.434\ 29\frac{e_x}{x} \tag{3-8}$$

Use relative uncertainty (e_x/x), not percent relative uncertainty [$100 \times (e_x/x)$], in calculations involving log x, ln x, 10^x, and e^x.

You should not work with percent relative uncertainty [$100 \times (e_x/x)$] in calculations with logs and antilogs, because one side of Equation 3-8 has relative uncertainty and the other has absolute uncertainty.

The **natural logarithm** (ln) of x is the number y, whose value is such that $x = e^y$, where e (= 2.718 28 . . .) is called the base of the natural logarithm. The absolute uncertainty in y is equal to the relative uncertainty in x.

Uncertainty for natural logarithm:

$$y = \ln x \quad \Rightarrow \quad e_y = \frac{e_x}{x} \tag{3-9}$$

Now consider y = antilog x, which is the same as saying $y = 10^x$. In this case, the relative uncertainty in y is proportional to the absolute uncertainty in x.

Box 3-2 Propagation of Uncertainty in the Product $x \cdot x$

Table 3-1 says that the uncertainty in the function $y = x^a$ is $\%e_y = a(\%e_x)$. If $y = x^2$, then $a = 2$ and $\%e_y = 2(\%e_x)$. A 3% uncertainty in x leads to a $(2)(3\%) = 6\%$ uncertainty in y.

But what if we just apply the multiplication formula 3-6 to the product $x \cdot x$?

$$x(\pm e_1) \cdot x(\pm e_2) = x^2(\pm e_3)$$

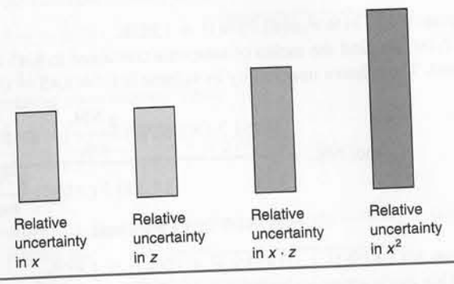
$$\%e_3 = \sqrt{(\%e_1)^2 + (\%e_2)^2} = \sqrt{(3\%)^2 + (3\%)^2} = 4._2\%$$

Which uncertainty is correct, 6% from Table 3-1 or $4._2$% from Equation 3-6?

Table 3-1 (6%) is correct. In the formula $y = x^2$, the error in a measured value of x is always positive or always negative. If the true value of x is 1.00 and the measured value is 1.01, the computed value of x^2 is $(1.01)^2 = 1.02$. That is, if the measured x is high by 1%, the computed value of x^2 is high by 2% because we are multiplying the high value by the high value.

Equation 3-6 presumes that the uncertainty in each factor of the product $x \cdot z$ is random and independent of the other. In the product $x \cdot z$, the measured value of x could be high sometimes and the measured value of z could be low sometimes. In the majority of cases, the uncertainty in the product $x \cdot z$ is not as great as the uncertainty in x^2.

Example. The distance traveled by a falling object in time t is $\frac{1}{2}gt^2$, where g is the acceleration of gravity. If t has an uncertainty of 1%, the uncertainty in t^2 is $2(\%e_t) = 2(1\%) = 2\%$. The uncertainty in distance computed from $\frac{1}{2}gt^2$ will also be 2%. If you (incorrectly) used Equation 3-6, you would compute an uncertainty in distance of $\sqrt{1\%^2 + 1\%^2} = 1._4\%$.



Uncertainty for 10^x:

$$y = 10^x \quad \Rightarrow \quad \frac{e_y}{y} = (\ln 10)e_x \approx 2.302\,6\,e_x \tag{3-10}$$

If $y = e^x$, the relative uncertainty in y equals the absolute uncertainty in x.

Uncertainty for e^x:

$$y = e^x \quad \Rightarrow \quad \frac{e_y}{y} = e_x \tag{3-11}$$

Table 3-1 summarizes rules for propagation of uncertainty. You need not memorize the rules for exponents, logs, and antilogs, but you should be able to use them.

Appendix C gives a general rule for propagation of random uncertainty for any function.

Example Uncertainty in H^+ Concentration

Consider the function $pH = -\log[H^+]$, where $[H^+]$ is the molarity of H^+. For $pH = 5.21 \pm 0.03$, find $[H^+]$ and its uncertainty.

Solution First solve the equation $pH = -\log[H^+]$ for $[H^+]$: Whenever $a = b$, then $10^a = 10^b$. If $pH = -\log[H^+]$, then $\log[H^+] = -pH$ and $10^{\log[H^+]} = 10^{-pH}$. But $10^{\log[H^+]} = [H^+]$. We therefore need to find the uncertainty in the equation

$$[H^+] = 10^{-pH} = 10^{-(5.21 \pm 0.03)}$$

In Table 3-1, the relevant function is $y = 10^x$, in which $y = [H^+]$ and $x = -(5.21 \pm 0.03)$. For $y = 10^x$, the table tells us that $e_y/y = 2.302\,6\,e_x$.

$$\frac{e_y}{y} = 2.302\,6\,e_x = (2.302\,6)(0.03) = 0.069\,1 \tag{3-12}$$

The relative uncertainty in y $(= e_y/y)$ is 0.069 1. Inserting the value $y = 10^{-5.21} = 6.17 \times 10^{-6}$ into Equation 3-12 gives the answer:

$$\frac{e_y}{y} = \frac{e_y}{6.17 \times 10^{-6}} = 0.069\,1 \quad \Rightarrow \quad e_y = 4.26 \times 10^{-7}$$

The concentration of H^+ is $6.17\ (\pm 0.426) \times 10^{-6} = 6.2\ (\pm 0.4) \times 10^{-6}$ M. An uncertainty of 0.03 in pH gives an uncertainty of 7% in $[H^+]$. Notice that extra digits were retained in the intermediate results and were not rounded off until the final answer.

Table 3-1 Summary of rules for propagation of uncertainty

Function	Uncertainty	Function[a]	Uncertainty[b]
$y = x_1 + x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = x^a$	$\%e_y = a\%e_x$
$y = x_1 - x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = \log x$	$e_y = \frac{1}{\ln 10}\frac{e_x}{x} \approx 0.434\,29\frac{e_x}{x}$
$y = x_1 \cdot x_2$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = \ln x$	$e_y = \frac{e_x}{x}$
$y = \frac{x_1}{x_2}$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = 10^x$	$\frac{e_y}{y} = (\ln 10)e_x \approx 2.302\,6\,e_x$
		$y = e^x$	$\frac{e_y}{y} = e_x$

a. x represents a variable and a represents a constant that has no uncertainty.

b. e_x/x is the relative error in x and $\%e_x$ is $100 \times e_x/x$.

3-5 Propagation of Uncertainty: Systematic Error

Systematic error occurs in some common situations and is treated differently from random error in arithmetic operations.

Uncertainty in Molecular Mass

What is the uncertainty in the molecular mass of O_2? On the inside cover of this book, we find that the atomic mass of oxygen is $15.999\,4 \pm 0.000\,3$ g/mol. The uncertainty is *not* mainly from random error in measuring the atomic mass. The uncertainty is predominantly from isotopic variation in samples of oxygen from different sources. That is, oxygen from one source could have a mean atomic mass of 15.999 1 and oxygen from another source could have an atomic mass of 15.999 7. The atomic mass of oxygen in a particular lot of reagent has a *systematic* uncertainty. It could be relatively constant at 15.999 7 or 15.999 1, or any value in between, with only a small random variation around the mean value.

If the true mass were 15.999 7, then the mass of O_2 is $2 \times 15.999\,7 = 31.999\,4$ g/mol. If the true mass is 15.999 1, then the mass of O_2 is $2 \times 15.999\,1 = 31.998\,2$ g/mol. The mass of O_2 is somewhere in the range $31.998\,8 \pm 0.000\,6$. The uncertainty of the mass of n atoms is $n \times$ (uncertainty of one atom) $= 2 \times (\pm 0.000\,3) = \pm 0.000\,6$. The uncertainty is not $\pm\sqrt{0.000\,3^2 + 0.000\,3^2} = \pm 0.000\,4_2$. For systematic uncertainty, we add the uncertainties of each term in a sum or difference.

Now let's find the molecular mass of C_2H_4:

$$\begin{aligned} 2C:\ & 2(12.010\,7 \pm 0.000\,8) = 24.021\,4 \pm 0.001\,6 \leftarrow 2 \times 0.000\,8 \\ 4H:\ & 4(1.007\,94 \pm 0.000\,07) = \underline{4.031\,76 \pm 0.000\,28} \leftarrow 4 \times 0.000\,07 \\ & 28.053\,16 \pm\ ? \end{aligned} \tag{3-13}$$

Propagation of systematic uncertainty: Uncertainty in mass of n identical atoms = $n \times$ (uncertainty in atomic mass).

For the uncertainty in the sum of the masses of 2C + 4H, we use Equation 3-5, which applies to random error, because the uncertainties in the masses of C and H are independent of each other. One might be positive and one might be negative. So the molecular mass of C_2H_4 is

$$28.053\,16 \pm \sqrt{0.001\,6^2 + 0.000\,28^2}$$

$$28.053\,16 \pm 0.001\,6$$

$$28.053 \pm 0.002\ \text{g/mol}$$

We choose to use the rule for propagation of random uncertainty for the sum of atomic masses of different elements.

Multiple Deliveries from One Pipet

A 25-mL Class A volumetric pipet is certified by the manufacturer to deliver 25.00 ± 0.03 mL. The volume delivered by a given pipet is reproducible, but can be anywhere in the range 24.97 to 25.03 mL. The difference between 25.00 mL and the actual volume delivered by a particular pipet is a *systematic* error. It is always the same, within a small random error. You could calibrate a pipet by weighing the water it delivers, as in Section 2-9.

Calibration eliminates systematic error, because we would know that the pipet always delivers, say, 25.991 ± 0.006 mL. The remaining uncertainty (±0.006 mL) is random error.

If you use an uncalibrated 25-mL Class A volumetric pipet four times to deliver a total of 100 mL, what is the uncertainty in 100 mL? Because the uncertainty is a systematic error, the uncertainty in four pipet volumes is like the uncertainty in the mass of 4 moles of oxygen: The uncertainty is $\pm 4 \times 0.03 = \pm 0.12$ mL, not $\pm\sqrt{0.03^2 + 0.03^2 + 0.03^2 + 0.03^2} = \pm 0.06$ mL.

this example, calibration reduces the ncertainty from ±0.12 mL to ±0.012 mL.

Calibration improves accuracy. Suppose that a calibrated pipet delivers a mean volume of 24.991 mL with a standard deviation (a random variation) of ±0.006 mL. If you deliver four aliquots from this pipet, the volume delivered is $4 \times 24.991 = 99.964$ mL and the uncertainty is $\pm\sqrt{0.006^2 + 0.006^2 + 0.006^2 + 0.006^2} = \pm 0.012$ mL.

erms to Understand

bsolute uncertainty
ccuracy
ntilogarithm
haracteristic
determinate error
indeterminate error
logarithm
mantissa
natural logarithm
precision
random error
relative uncertainty
significant figure
systematic error

Summary

The number of significant digits in a number is the minimum required to write the number in scientific notation. The first uncertain digit is the last significant figure. In addition and subtraction, the last significant figure is determined by the number with the fewest decimal places (when all exponents are equal). In multiplication and division, the number of figures is usually limited by the factor with the smallest number of digits. The number of figures in the mantissa of the logarithm of a quantity should equal the number of significant figures in the quantity. Random (indeterminate) error affects the precision (reproducibility) of a result, whereas systematic (determinate) error affects the accuracy (nearness to the "true" value). Systematic error can be discovered and eliminated by a clever person, but some random error is always present. For random errors, propagation of uncertainty in addition and subtraction requires absolute uncertainties ($e_3 = \sqrt{e_1^2 + e_2^2}$), whereas multiplication and division utilize relative uncertainties ($\%e_3 = \sqrt{\%e_1^2 + e_2^2}$). Other rules for propagation of random error are found in Table 3-1. Always retain more digits than necessary during a calculation and round off to the appropriate number of digits at the end. Systematic error in atomic mass or the volume of a pipet leads to larger uncertainty than we get from random error. We always strive to eliminate systematic errors.

Exercises

3-A. Write each answer with a reasonable number of figures. Find the absolute and percent relative uncertainty for each answer.
(a) [12.41 (±0.09) ÷ 4.16 (±0.01)] × 7.068 2 (±0.000 4) = ?
(b) [3.26 (±0.10) × 8.47 (±0.05)] − 0.18 (±0.06) = ?
(c) 6.843 (±0.008) × 10^4 ÷ [2.09 (±0.04) − 1.63 (±0.01)] = ?
(d) $\sqrt{3.24 \pm 0.08}$ = ?
(e) $(3.24 \pm 0.08)^4$ = ?
(f) log(3.24 ± 0.08) = ?
(g) $10^{3.24 \pm 0.08}$ = ?

3-B. (a) You have a bottle labeled "53.4 (±0.4) wt% NaOH—density = 1.52 (±0.01) g/mL." How many milliliters of 53.4 wt% NaOH will you need to prepare 2.000 L of 0.169 M NaOH? (b) If the uncertainty in delivering NaOH is ±0.01 mL, calculate the absolute uncertainty in the molarity (0.169 M). Assume there is negligible uncertainty in the formula mass of NaOH and in the final volume (2.000 L).

3-C. We have a 37.0 (±0.5) wt% HCl solution with a density of 1.18 (±0.01) g/mL. To deliver 0.050 0 mol of HCl requires 4.18 mL of solution. If the uncertainty that can be tolerated in 0.050 0 mol is ±2%, how big can the absolute uncertainty in 4.18 mL be? (*Caution:* In this problem, you have to work backward. You would normally compute the uncertainty in mol HCl from the uncertainty in volume:

$$\text{mol HCl} = \frac{\text{mL solution} \times \dfrac{\text{g solution}}{\text{mL solution}} \times \dfrac{\text{g HCl}}{\text{g solution}}}{\dfrac{\text{g HCl}}{\text{mol HCl}}}$$

But, in this case, we know the uncertainty in mol HCl (2%) and we need to find what uncertainty in mL solution leads to that 2% uncertainty. The arithmetic has the form $a = b \times c \times d$, for which $\%e_a^2 = \%e_b^2 + \%e_c^2 + \%e_d^2$. If we know $\%e_a$, $\%e_c$, and $\%e_d$, we can find $\%e_b$ by subtraction: $\%e_b^2 = \%e_a^2 - \%e_c^2 - \%e_d^2$.)

Problems

Significant Figures

3-1. How many significant figures are there in the following numbers?
(a) 1.903 0 (b) 0.039 10 (c) 1.40×10^4

3-2. Round each number as indicated:
(a) 1.236 7 to 4 significant figures
(b) 1.238 4 to 4 significant figures
(c) 0.135 2 to 3 significant figures
(d) 2.051 to 2 significant figures
(e) 2.005 0 to 3 significant figures

3-3. Round each number to three significant figures:
(a) 0.216 74
(b) 0.216 5
(c) 0.216 500 3

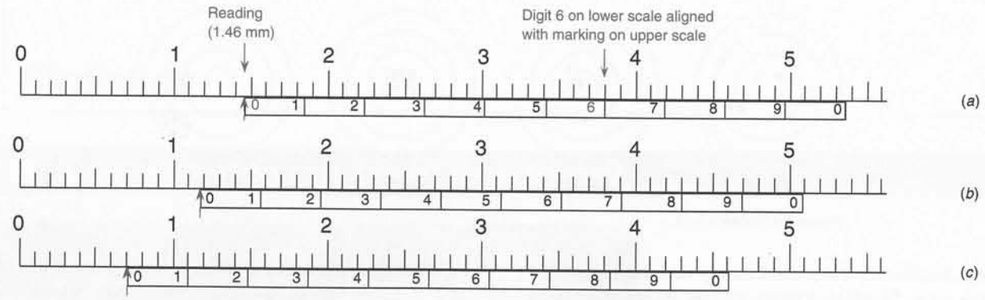


Figure for Problem 3-4.

3-4. *Vernier scale.* The figure above shows a scale found on instruments such as a micrometer caliper used for accurately measuring dimensions of objects. The lower scale slides along the upper scale and is used to interpolate between the markings on the upper scale. In (*a*), the reading (at the left-hand 0 of the lower scale) is between 1.4 and 1.5 on the upper scale. To find the exact reading, observe which mark on the lower scale is aligned with a mark on the upper scale. Because the 6 on the lower scale is aligned with the upper scale, the correct reading is 1.46. Write the correct readings in (*b*) and (*c*) and indicate how many significant figures are in each reading.

3-5. Write each answer with the correct number of digits.
(a) 1.021 + 2.69 = 3.711
(b) 12.3 − 1.63 = 10.67
(c) 4.34 × 9.2 = 39.928
(d) 0.060 2 ÷ (2.113 × 10^4) = 2.849 03 × 10^{-6}
(e) log(4.218 × 10^{12}) = ?
(f) antilog(−3.22) = ?
(g) $10^{2.384}$ = ?

3-6. Write the formula mass of (a) BaF_2 and (b) $C_6H_4O_4$ with a reasonable number of digits. Use the periodic table inside the cover of this book to find atomic masses.

3-7. Write each answer with the correct number of significant figures.
(a) 1.0 + 2.1 + 3.4 + 5.8 = 12.300 0
(b) 106.9 − 31.4 = 75.500 0
(c) 107.868 − (2.113 × 10^2) + (5.623 × 10^3) = 5 519.568
(d) (26.14/37.62) × 4.38 = 3.043 413
(e) (26.14/(37.62 × 10^8)) × (4.38 × 10^{-2}) = 3.043 413 × 10^{-10}
(f) (26.14/3.38) + 4.2 = 11.933 7
(g) log(3.98 × 10^4) = 4.599 9
(h) $10^{-6.31}$ = 4.897 79 × 10^{-7}

3-8. *Controlling the appearance of a graph in Excel.* Figure 3-3 requires gridlines to read the graph for buret corrections. The purpose of this exercise is to format a graph so it looks like Figure 3-3. Follow the procedure in Section 2-11 to make a graph of the data in the following table. The Chart Type is xy Scatter showing data points connected by straight lines. Double click on the x-axis and select the Scale tab. Set Minimum = 0, Maximum = 50, Major unit = 10, and Minor unit = 1. Select the Number tab and highlight Number. Set Decimal places = 0. In a similar manner, set the ordinate to run from −0.04 to +0.05 with a major unit of 0.02 and a minor unit of 0.01, as in Figure 3-3. The spreadsheet may overrule you several times. Continue to reset the limits as you want them and click OK each time until the graph looks the way you intend. To add gridlines, click in the graph, go to the CHART menu and select CHART OPTIONS. Select the Gridlines tab and check both sets of Major gridlines and Minor gridlines and click OK. In the CHART OPTIONS menu, select the Legend tab and deselect Show legend. Move the x-axis numbers from the middle of the chart to the bottom as follows: Double click the y-axis (not the x-axis) and select the Scale tab. Set "Value (x) axis crosses at" to −0.04. Click OK and the volume labels move beneath the graph. Your graph should look the same as Figure 3-3.

Volume (mL)	Correction (mL)
0.03	0.00
10.04	0.04
20.03	0.02
29.98	−0.03
40.00	0.00
49.97	0.03

Types of Error

3-9. Why do we use quotation marks around the word *true* in the statement that accuracy refers to how close a measured value is to the "true" value?

3-10. Explain the difference between systematic and random errors.

3-11. Suppose that in a gravimetric analysis, you forget to dry the filter crucibles before collecting precipitate. After filtering the product, you dry the product and crucible thoroughly before weighing them. Is the mass of product always high or always low? Is the error in mass systematic or random?

3-12. State whether the errors in parts **(a)–(d)** are random or systematic:
(a) A 25-mL transfer pipet consistently delivers 25.031 ± 0.009 mL.
(b) A 10-mL buret consistently delivers 1.98 ± 0.01 mL when drained from exactly 0 to exactly 2 mL and consistently delivers 2.03 mL ± 0.02 mL when drained from 2 to 4 mL.
(c) A 10-mL buret delivered 1.983 9 g of water when drained from exactly 0.00 to 2.00 mL. The next time I delivered water from the 0.00- to the 2.00-mL mark, the delivered mass was 1.990 0 g.
(d) Four consecutive 20.0-μL injections of a solution into a chromatograph were made and the area of a particular peak was 4 383, 4 410, 4 401, and 4 390 units.

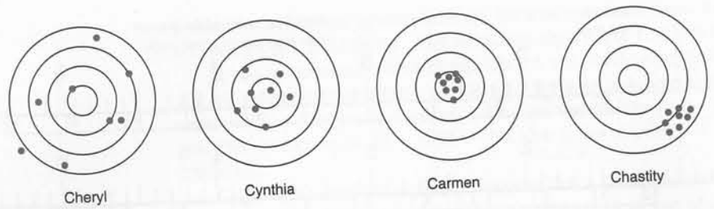


Figure for Problem 3-13.

3-13. Cheryl, Cynthia, Carmen, and Chastity shot the targets above at Girl Scout camp. Match each target with the proper description.
(a) accurate and precise
(b) accurate but not precise
(c) precise but not accurate
(d) neither precise nor accurate

3-14. Rewrite the number 3.123 56 (±0.167 89%) in the forms (a) number (±absolute uncertainty) and (b) number (±percent relative uncertainty) with an appropriate number of digits.

Propagation of Uncertainty

3-15. Find the absolute and percent relative uncertainty and express each answer with a reasonable number of significant figures.
(a) 6.2 (±0.2) − 4.1 (±0.1) = ?
(b) 9.43 (±0.05) × 0.016 (±0.001) = ?
(c) [6.2 (±0.2) − 4.1 (±0.1)] ÷ 9.43 (±0.05) = ?
(d) $9.43\,(\pm 0.05) \times \{[6.2\,(\pm 0.2) \times 10^{-3}] + [4.1\,(\pm 0.1) \times 10^{-3}]\} = ?$

3-16. Find the absolute and percent relative uncertainty and express each answer with a reasonable number of significant figures.
(a) 9.23 (±0.03) + 4.21 (±0.02) − 3.26 (±0.06) = ?
(b) 91.3 (±1.0) × 40.3 (±0.2)/21.1 (±0.2) = ?
(c) [4.97 (±0.05) − 1.86 (±0.01)]/21.1 (±0.2) = ?
(d) 2.016 4 (±0.000 8) + 1.233 (±0.002) + 4.61 (±0.01) = ?
(e) $2.016\,4\,(\pm 0.000\,8) \times 10^3 + 1.233\,(\pm 0.002) \times 10^2 + 4.61\,(\pm 0.01) \times 10^1 = ?$
(f) $[3.14\,(\pm 0.05)]^{1/3} = ?$
(g) log[3.14 (±0.05)] = ?

3-17. Verify the following calculations:
(a) $\sqrt{3.141\,5\,(\pm 0.001\,1)} = 1.772\,4_3\,(\pm 0.000\,3_1)$
(b) $\log[3.141\,5\,(\pm 0.001\,1)] = 0.497\,1_4\,(\pm 0.000\,1_5)$
(c) $\text{antilog}[3.141\,5\,(\pm 0.001\,1)] = 1.385_2(\pm 0.003_5) \times 10^3$
(d) $\ln[3.141\,5\,(\pm 0.001\,1)] = 1.144\,7_0(\pm 0.000\,3_5)$
(e) $\log\left(\dfrac{\sqrt{0.104\,(\pm 0.006)}}{0.051\,1\,(\pm 0.000\,9)}\right) = 0.80_0\,(\pm 0.01_5)$

3-18. Express the molecular mass (±uncertainty) of $C_9H_9O_6N_3$ with the correct number of significant figures.

3-19. (a) Show that the formula mass of NaCl is 58.443 (±0.002) g/mol.

(b) To prepare a solution of NaCl, you weigh out 2.634 (±0.002) g and dissolve it in a volumetric flask whose volume is 100.00 (±0.08) mL. Express the molarity of the solution, along with its uncertainty, with an appropriate number of digits.

3-20. What is the true mass of water weighed at 24°C in the air if the apparent mass is $1.034\,6 \pm 0.000\,2$ g? The density of air is $0.001\,2 \pm 0.000\,1$ g/mL and the density of balance weights is 8.0 ± 0.5 g/mL. The uncertainty in the density of water in Table 2-7 is negligible in comparison to the uncertainty in the density of air.

3-21. Twelve dietary iron tablets were analyzed by the gravimetric procedure in Section 1-4 and the final mass of Fe_2O_3 (FM 159.688) was $0.277_4 \pm 0.001_8$ g. Find the average mass of Fe per tablet. (Relative uncertainties in atomic masses are small compared with relative uncertainty in the mass of Fe_2O_3. Neglect uncertainties in atomic masses in this problem.)

3-22. We can measure the concentration of HCl solution (a procedure called *standardizing* the solution) by reaction with pure sodium carbonate: $2H^+ + Na_2CO_3 \rightarrow 2Na^+ + H_2O + CO_2$. A volume of 27.35 ± 0.04 mL of HCl solution was required for complete reaction with $0.967\,4 \pm 0.000\,9$ g of Na_2CO_3 (FM 105.988 ± 0.001). Find the molarity of the HCl and its absolute uncertainty.

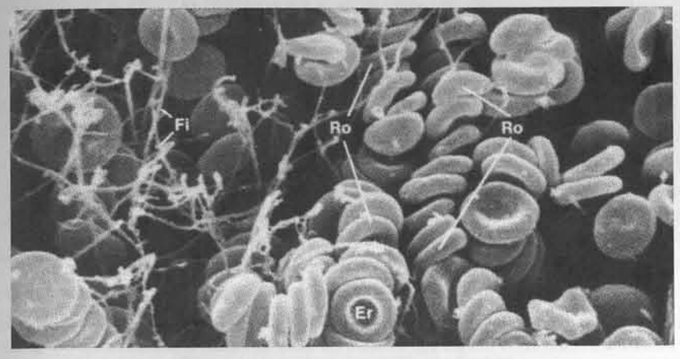
3-23. Avogadro's number can be computed from the following measured properties of pure crystalline silicon:[2] (1) atomic mass (obtained from the mass and abundance of each isotope), (2) density of the crystal, (3) size of the unit cell (the smallest repeating unit in the crystal), and (4) number of atoms in the unit cell. For silicon, the mass is $m_{Si} = 28.085\,384\,2\,(35)$ g/mol, where 35 is the standard deviation in the last two digits. The density is $\rho = 2.329\,031\,9\,(18)$ g/cm³, the size of the cubic unit cell is $c_0 = 5.431\,020\,36\,(33) \times 10^{-8}$ cm, and there are 8 atoms per unit cell. Avogadro's number is computed from the equation

$$N_A = \frac{m_{Si}}{(\rho c_0^3)/8}$$

From the measured properties and their uncertainties (standard deviations), compute Avogadro's number and its uncertainty. To find the uncertainty of c_0^3, use the function $y = x^a$ in Table 3-1.

4 Statistics

IS MY RED BLOOD CELL COUNT HIGH TODAY?



Red blood cells (erythrocytes, Er) tangled in fibrin threads (Fi) in a blood clot. Stacks of erythrocytes in a clot are called a rouleaux formation (Ro). *[From R. H. Kardon, Tissues and Organs (San Francisco: W. H. Freeman, 1978), p. 39.]*

All measurements contain experimental error, so it is never possible to be completely certain of a result. Nevertheless, we often seek the answers to questions such as "Is my red blood cell count today higher than usual?" If today's count is twice as high as usual, it is probably truly higher than normal. But what if the "high" count is not excessively above "normal" counts?

Count on "normal" days	Today's count
5.1 5.3 4.8 5.4 5.2 } × 10^6 cells/μL	5.6×10^6 cells/μL

The number 5.6 is higher than the five normal values, but the random variation in normal values might lead us to expect that 5.6 will be observed on some "normal" days.

The study of statistics allows us to say that today's value is expected to be observed on 1 out of 20 normal days. It is still up to you to decide what to do with this information.

Experimental measurements always contain some variability, so no conclusion can be drawn with certainty. Statistics gives us tools to accept conclusions that have a high probability of being correct and to reject conclusions that do not.[1,2]

4-1 Gaussian Distribution

If an experiment is repeated a great many times and if the errors are purely random, then the results tend to cluster symmetrically about the average value (Figure 4-1). The more times the experiment is repeated, the more closely the results approach an ideal smooth curve called the **Gaussian distribution.** In general, we cannot make so many measurements in a lab experiment. We are more likely to repeat an experiment 3 to 5 times than 2 000 times. However, from the small set of results, we can estimate the statistical parameters that describe the large set. We can then make estimates of statistical behavior from the small number of measurements.

We say that the variation in experimental data is *normally distributed* when replicate measurements exhibit the bell-shaped distribution in Figure 4-1. It is equally probable that a measurement will be higher or lower than the mean. The probability of observing any value decreases as its distance from the mean increases.

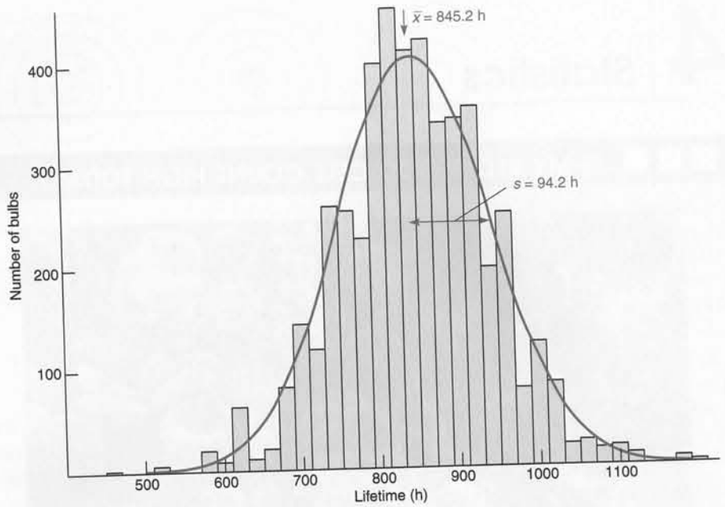


Figure 4-1 Bar graph and Gaussian curve describing the lifetimes of a hypothetical set of electric light bulbs. The smooth curve has the same mean, standard deviation, and area as the bar graph. Any finite set of data, however, will differ from the bell-shaped curve. The more measurements an investigator makes, the closer they will come to the smooth curve.

The mean gives the center of the distribution. The standard deviation measures the width of the distribution.

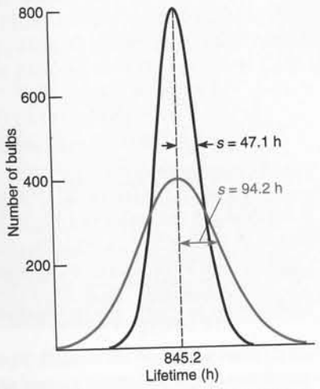


Figure 4-2 Gaussian curves for two sets of light bulbs, one having a standard deviation half as great as the other. The number of bulbs described by each curve is the same.

An experiment that produces a small standard deviation is more *precise* than one that produces a large standard deviation. Greater precision does not necessarily imply greater *accuracy*, which means nearness to the "truth."

As the number of measurements increases, $\bar{x}$ approaches μ, *if there is no systematic error.*

Mean Value and Standard Deviation

In the hypothetical case in Figure 4-1, a manufacturer tested the lifetimes of 4 768 electric light bulbs. The bar graph shows the number of bulbs with a lifetime in each 20-h interval. Lifetimes approximate a Gaussian distribution because variations in the construction of light bulbs, such as filament thickness and quality of attachments, are random. The smooth curve is the Gaussian distribution that best fits the data. Any finite set of data will vary somewhat from the Gaussian curve.

Light bulb lifetimes, and the corresponding Gaussian curve, are characterized by two parameters. The arithmetic **mean,** $\bar{x}$—also called the **average**—is the sum of the measured values divided by n, the number of measurements:

Mean:
$$\bar{x} = \frac{\sum_i x_i}{n} \tag{4-1}$$

where x_i is the lifetime of an individual bulb. The Greek capital sigma, Σ, means summation: $\Sigma_i x_i = x_1 + x_2 + x_3 + \cdots + x_n$. In Figure 4-1, the mean value is 845.2 h.

The **standard deviation,** s, measures how closely the data are clustered about the mean. *The smaller the standard deviation, the more closely the data are clustered about the mean* (Figure 4-2).

Standard deviation:
$$s = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n - 1}} \tag{4-2}$$

In Figure 4-1, s = 94.2 h. A set of light bulbs having a small standard deviation in lifetime is more uniformly manufactured than a set with a large standard deviation.

For an *infinite* set of data, the mean is designated by the lowercase Greek letter mu, μ (the population mean), and the standard deviation is written as a lowercase Greek sigma, σ (the population standard deviation). We can never measure μ and σ, but the values of $\bar{x}$ and s approach μ and σ as the number of measurements increases.

The quantity $n - 1$ in Equation 4-2 is called the **degrees of freedom.** The square of the standard deviation is called the **variance.** The standard deviation expressed as a percentage of the mean value ($= 100 \times s/\bar{x}$) is called the *relative standard deviation* or the *coefficient of variation*.

Example Mean and Standard Deviation

Find the average and the standard deviation for 821, 783, 834, and 855.

Solution The average is

$$\bar{x} = \frac{821 + 783 + 834 + 855}{4} = 823._2$$

To avoid accumulating round-off errors, retain one more digit for the average and the standard deviation than was present in the original data. The standard deviation is

$$s = \sqrt{\frac{(821 - 823.2)^2 + (783 - 823.2)^2 + (834 - 823.2)^2 + (855 - 823.2)^2}{(4 - 1)}} = 30._3$$

The average and the standard deviation should both end at the *same decimal place*. For $\bar{x} = 823._2$, we will write $s = 30._3$.

Spreadsheets have built-in functions for the average and standard deviation. In the spreadsheet in the margin, data points are entered in cells B1 through B4. The average in cell B5 is computed with the statement "= AVERAGE(B1:B4)". B1:B4 means cells B1, B2, B3, and B4. The standard deviation in cell B6 is computed with "= STDEV(B1:B4)".

For ease of reading, cells B5 and B6 were set to display 3 decimal places by use of the CELLS command in the FORMAT menu. A heavy line was placed beneath cell B4 by setting border with the CELLS command of the FORMAT menu.

Learn to use the standard deviation function on your calculator and see that you get $s = 30.269\,6\ldots$. Do not round off during a calculation. Retain all the extra digits in your calculator.

	A	B
1		821
2		783
3		834
4		855
5	Average =	823.250
6	Std dev =	30.270

Significant Figures in Mean and Standard Deviation

We commonly express experimental results in the form: mean $\pm$ standard deviation $= \bar{x} \pm s$. It is sensible to write the results of the preceding example as 823 ± 30 or even $8.2\ (\pm 0.3) \times 10^2$ to indicate that the mean has just two significant figures. The expressions 823 ± 30 and $8.2\ (\pm 0.3) \times 10^2$ are not suitable for continued calculations in which $\bar{x}$ and s are intermediate results. We will retain one or more insignificant digits to avoid introducing round-off errors into subsequent work. Try not to go into cardiac arrest over significant figures when you see $823._2 \pm 30._3$ as the answer to a problem in this book.

Standard Deviation and Probability

The formula for a Gaussian curve is

Gaussian curve:
$$y = \frac{1}{\sigma\sqrt{2\pi}}\, e^{-(x-\mu)^2/2\sigma^2} \tag{4-3}$$

where e ($= 2.718\,28\ldots$) is the base of the natural logarithm. For a finite set of data, we approximate μ by $\bar{x}$ and σ by s. A graph of Equation 4-3 is shown in Figure 4-3, in which the values $\sigma = 1$ and $\mu = 0$ are used for simplicity. The maximum value of y is at $x = \mu$, and the curve is symmetric about $x = \mu$.

It is useful to express deviations from the mean value in multiples, z, of the standard deviation. That is, we transform x into z, given by

$$z = \frac{x - \mu}{\sigma} \approx \frac{x - \bar{x}}{s} \tag{4-4}$$

The probability of measuring z in a certain *range* is equal to the *area* of that range. For example, the probability of observing z between -2 and -1 is 0.136. This probability corresponds to the shaded area in Figure 4-3. The area under each portion of the Gaussian curve is given in Table 4-1. Because the sum of the probabilities of all the measurements must be unity, the area under the whole curve from $z = -\infty$ to $z = +\infty$ must be unity. The number $1/(\sigma\sqrt{2\pi})$ in Equation 4-3 is called the *normalization factor*. It guarantees that the area under the entire curve is unity. A Gaussian curve with unit area is called a *normal error curve*.

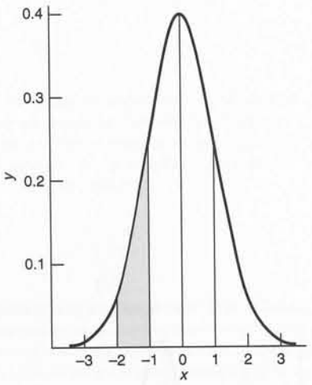


Figure 4-3 A Gaussian curve in which $\mu = 0$ and $\sigma = 1$. A Gaussian curve whose area is unity is called a normal error curve. In this case, the abscissa, x, is equal to z, defined as $z = (x - \mu)/\sigma$.

When $z = +1$, x is one standard deviation above the mean. When $z = -2$, x is two standard deviations below the mean.

Example Area Under a Gaussian Curve

Suppose the manufacturer of the bulbs used for Figure 4-1 offers to replace free of charge any bulb that burns out in less than 600 hours. If she plans to sell a million bulbs, how many extra bulbs should she keep available as replacements?

Table 4-1 Ordinate and area for the normal (Gaussian) error curve, $y = \frac{1}{\sqrt{2\pi}} e^{-z^2/2}$

$\lvert z\rvert$[a]	y	Area[b]	$\lvert z\rvert$	y	Area	$\lvert z\rvert$	y	Area
0.0	0.398 9	0.000 0	1.4	0.149 7	0.419 2	2.8	0.007 9	0.497 4
0.1	0.397 0	0.039 8	1.5	0.129 5	0.433 2	2.9	0.006 0	0.498 1
0.2	0.391 0	0.079 3	1.6	0.110 9	0.445 2	3.0	0.004 4	0.498 650
0.3	0.381 4	0.117 9	1.7	0.094 1	0.455 4	3.1	0.003 3	0.499 032
0.4	0.368 3	0.155 4	1.8	0.079 0	0.464 1	3.2	0.002 4	0.499 313
0.5	0.352 1	0.191 5	1.9	0.065 6	0.471 3	3.3	0.001 7	0.499 517
0.6	0.333 2	0.225 8	2.0	0.054 0	0.477 3	3.4	0.001 2	0.499 663
0.7	0.312 3	0.258 0	2.1	0.044 0	0.482 1	3.5	0.000 9	0.499 767
0.8	0.289 7	0.288 1	2.2	0.035 5	0.486 1	3.6	0.000 6	0.499 841
0.9	0.266 1	0.315 9	2.3	0.028 3	0.489 3	3.7	0.000 4	0.499 904
1.0	0.242 0	0.341 3	2.4	0.022 4	0.491 8	3.8	0.000 3	0.499 928
1.1	0.217 9	0.364 3	2.5	0.017 5	0.493 8	3.9	0.000 2	0.499 952
1.2	0.194 2	0.384 9	2.6	0.013 6	0.495 3	4.0	0.000 1	0.499 968
1.3	0.171 4	0.403 2	2.7	0.010 4	0.496 5	∞	0	0.5

a. $z = (x - \mu)/\sigma$.

b. The area refers to the area between $z = 0$ and $z =$ the value in the table. Thus the area from $z = 0$ to $z = 1.4$ is 0.419 2. The area from $z = -0.7$ to $z = 0$ is the same as from $z = 0$ to $z = 0.7$. The area from $z = -0.5$ to $z = +0.3$ is (0.191 5 + 0.117 9) = 0.309 4. The total area between $z = -\infty$ and $z = +\infty$ is unity.

Solution We need to express the desired interval in multiples of the standard deviation and then find the area of the interval in Table 4-1. Because $\bar{x} = 845.2$ and $s = 94.2$, $z = (600 - 845.2)/94.2 = -2.60$. The area under the curve between the mean value and $z = -2.60$ is 0.495 3 in Table 4-1. The entire area from $-\infty$ to the mean value is 0.500 0, so the area from $-\infty$ to -2.60 must be 0.500 0 − 0.495 3 = 0.004 7. The area to the left of 600 hours in Figure 4-1 is only 0.47% of the entire area under the curve. Only 0.47% of the bulbs are expected to fail in fewer than 600 h. If the manufacturer sells 1 million bulbs a year, she should make 4 700 extra bulbs to meet the replacement demand.

Example Using a Spreadsheet to Find Area Beneath a Gaussian Curve

What fraction of bulbs is expected to have a lifetime between 900 and 1 000 h?

Solution *We need to find the fraction of the area of the Gaussian curve between $x = 900$ and $x = 1\,000$ h.* The function NORMDIST in Excel gives the area of the curve from $-\infty$ up to a specified point, x. Here is the strategy: We will find the area from $-\infty$ to 900 h, which is the shaded area to the left of 900 h in Figure 4-4. Then we will find the area from $-\infty$ to 1 000 h, which is all the shaded area to the left of 1 000 h in Figure 4-4. The difference between the two is the area from 900 to 1 000 h:

$$\text{Area from 900 to 1 000} = (\text{area from } -\infty \text{ to 1 000}) - (\text{area from } -\infty \text{ to 900}) \quad (4\text{-}5)$$

In a spreadsheet, enter the mean in cell A2 and the standard deviation in cell B2. To find the area under the Gaussian curve from $-\infty$ to 900 h in cell C4, we select cell C4 and go to the INSERT menu and choose FUNCTION. In the window that appears, select the Statistical functions and find NORMDIST from the list of possibilities. Double click on NORMDIST and another window appears asking for four values that will be used by NORMDIST. (If you click on help, you will find a cryptic explanation of how to use NORMDIST.)

Values provided to the function NORMDIST(x,mean,standard_dev,cumulative) are called *arguments* of the function. The first argument is x, which is 900. The second argument is the mean, which is 845.2. You can either enter 845.2 for the mean or you can type "A2", which is the cell containing 845.2. The third argument is the standard deviation, for which we enter the value 94.2 or the cell B2. The last argument is called "cumulative." When it has the value TRUE, NORMDIST gives the area under the Gaussian curve. When cumulative is FALSE, NORMDIST gives the ordinate (the y-value) of the Gaussian curve. We want area, so enter TRUE. The formula "= NORMDIST(900,$A$2,$B$2,TRUE)" in cell C4

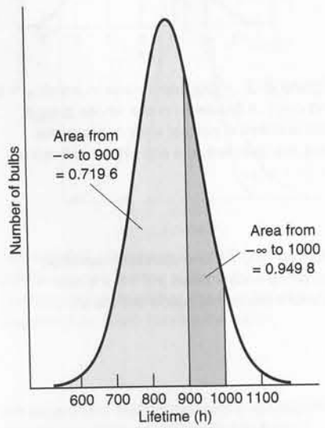


Figure 4-4 Use of the Gaussian curve to find the fraction of bulbs with a lifetime between 900 and 1 000 h. We find the area between $-\infty$ and 1 000 h and subtract the area between $-\infty$ and 900 h.

	A	B	C
1	Mean =	Std dev =	
2	845.2	94.2	
3			
4	Area from −∞ to 900 =		0.7196
5	Area from −∞ to 1000 =		0.9498
6	Area from 900 to 1000		0.2302
7			
8	C4 = NORMDIST(900,A2,B2,TRUE)		
9	C5 = NORMDIST(1000,A2,B2,TRUE)		
10	C6 = C5-C4		

returns the value 0.719 6. This is the area under the Gaussian curve from $-\infty$ to 900 h. To get the area from $-\infty$ to 1 000 h, write "= NORMDIST(1000,$A$2,$B$2,TRUE)" in cell C5. The value returned is 0.949 8. Following Equation 4-5, subtract the areas (C5 − C4) to obtain 0.230 2, which is the area from 900 to 1 000. That is, 23.02% of the area lies in the range 900 to 1 000 h. We expect 23% of the bulbs to have a lifetime of 900 to 1 000 h.

The standard deviation measures the width of the Gaussian curve. The larger the value of σ, the broader the curve. In any Gaussian curve, 68.3% of the area is in the range from $\mu - 1\sigma$ to $\mu + 1\sigma$. That is, more than two-thirds of the measurements are expected to lie within one standard deviation of the mean. Also, 95.5% of the area lies within $\mu \pm 2\sigma$, and 99.7% of the area lies within $\mu \pm 3\sigma$. Suppose that you use two different techniques to measure sulfur in coal: Method A has a standard deviation of 0.4%, and method B has a standard deviation of 1.1%. You can expect that approximately two-thirds of measurements from method A will lie within 0.4% of the mean. For method B, two-thirds will lie within 1.1% of the mean.

Range	Percentage of measurements
$\mu \pm 1\sigma$	68.3
$\mu \pm 2\sigma$	95.5
$\mu \pm 3\sigma$	99.7

The more times you measure a quantity, the more confident you can be that the average value of your measurements is close to the true population mean, μ. Uncertainty decreases in proportion to $1/\sqrt{n}$, where n is the number of measurements. You can decrease the uncertainty of the mean by a factor of 2 ($= \sqrt{4}$) by making 4 times as many measurements and by a factor of 3.16 ($= \sqrt{10}$) by making 10 times as many measurements.

To decrease uncertainty by $1/\sqrt{10}$ requires 10 measurements. Instruments with rapid data acquisition allow us to average many experiments in a short time to increase the accuracy of a result.

4-2 Confidence Intervals

Student's *t* is a statistical tool used most frequently to express confidence intervals and to compare results from different experiments. It is the tool you could use to evaluate the probability that your red blood cell count will be found in a certain range on "normal" days.

Calculating Confidence Intervals

From a limited number of measurements, we cannot find the true population mean, μ, or the true standard deviation, σ. What we can determine are $\bar{x}$ and s, the sample mean and the sample standard deviation. The **confidence interval** is an expression stating that the true mean, μ, is likely to lie within a certain distance from the measured mean, $\bar{x}$. The confidence interval of μ is given by

Confidence interval:
$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}} \quad (4\text{-}6)$$

where s is the measured standard deviation, n is the number of observations, and t is Student's t, taken from Table 4-2.

Example Calculating Confidence Intervals

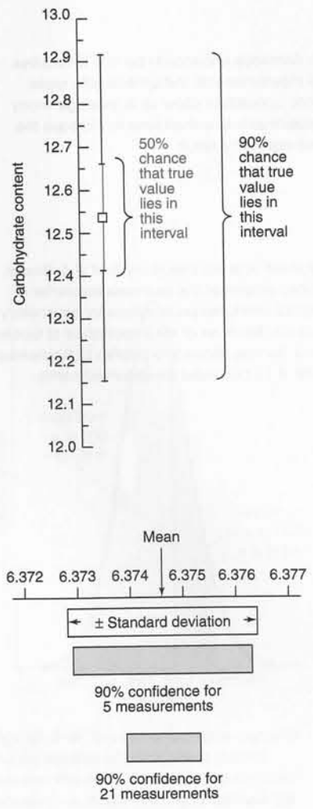
The carbohydrate content of a glycoprotein (a protein with sugars attached to it) is determined to be 12.6, 11.9, 13.0, 12.7, and 12.5 g of carbohydrate per 100 g of protein in replicate analyses. Find the 50% and 90% confidence intervals for the carbohydrate content.

"Student" was the pseudonym of W. S. Gosset, whose employer, the Guinness breweries of Ireland, restricted publications for proprietary reasons. Because of the importance of Gosset's work, he was allowed to publish it (*Biometrika* **1908**, *6*, 1), but under an assumed name.

Table 4-2 Values of Student's *t*

	Confidence level (%)						
Degrees of freedom	50	90	95	98	99	99.5	99.9
1	1.000	6.314	12.706	31.821	63.656	127.321	636.578
2	0.816	2.920	4.303	6.965	9.925	14.089	31.598
3	0.765	2.353	3.182	4.541	5.841	7.453	12.924
4	0.741	2.132	2.776	3.747	4.604	5.598	8.610
5	0.727	2.015	2.571	3.365	4.032	4.773	6.869
6	0.718	1.943	2.447	3.143	3.707	4.317	5.959
7	0.711	1.895	2.365	2.998	3.500	4.029	5.408
8	0.706	1.860	2.306	2.896	3.355	3.832	5.041
9	0.703	1.833	2.262	2.821	3.250	3.690	4.781
10	0.700	1.812	2.228	2.764	3.169	3.581	4.587
15	0.691	1.753	2.131	2.602	2.947	3.252	4.073
20	0.687	1.725	2.086	2.528	2.845	3.153	3.850
25	0.684	1.708	2.060	2.485	2.787	3.078	3.725
30	0.683	1.697	2.042	2.457	2.750	3.030	3.646
40	0.681	1.684	2.021	2.423	2.704	2.971	3.551
60	0.679	1.671	2.000	2.390	2.660	2.915	3.460
120	0.677	1.658	1.980	2.358	2.617	2.860	3.373
∞	0.674	1.645	1.960	2.326	2.576	2.807	3.291

NOTE: In calculating confidence intervals, σ may be substituted for s in Equation 4-6 if you have a great deal of experience with a particular method and have therefore determined its "true" population standard deviation. If σ is used instead of s, the value of t to use in Equation 4-6 comes from the bottom row of Table 4-2.



Solution First calculate $\bar{x}$ ($= 12.5_4$) and s ($= 0.4_0$) for the five measurements. For the 50% confidence interval, look up t in Table 4-2 under 50 and across from *four* degrees of freedom (degrees of freedom $= n - 1$.) The value of t is 0.741, so the 50% confidence interval is

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}} = 12.5_4 \pm \frac{(0.741)(0.4_0)}{\sqrt{5}} = 12.5_4 \pm 0.1_3$$

The 90% confidence interval is

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}} = 12.5_4 \pm \frac{(2.132)(0.4_0)}{\sqrt{5}} = 12.5_4 \pm 0.3_8$$

There is a 50% chance that the true mean, μ, lies within the range $12.5_4 \pm 0.1_3$ (12.4_1 to 12.6_7). There is a 90% chance that μ lies within the range $12.5_4 \pm 0.3_8$ (12.1_6 to 12.9_2).

Confidence Intervals as Estimates of Experimental Uncertainty

Chapter 3 gave rules for propagation of uncertainty in calculations. For example, if we were dividing a mass by a volume to find density, the uncertainty in density is derived from the uncertainties in mass and volume. The most common estimates of uncertainty are the standard deviation and the confidence interval.

Suppose you measure the volume of a vessel five times and observe values of 6.375, 6.372, 6.374, 6.377, and 6.375 mL. The average is $\bar{x} = 6.374_6$ mL and the standard deviation is $s = 0.001_8$ mL. You could choose a confidence interval (such as 90%) for the estimate of uncertainty. Using Equation 4-6 with four degrees of freedom, you find that the 90% confidence interval is $\pm ts/\sqrt{n} = \pm(2.132)(0.001_8)/\sqrt{5} = \pm 0.001_7$. By this criterion, the uncertainty in volume is $\pm 0.001_7$ mL.

We can reduce uncertainty by making more measurements. If we make 21 measurements and have the same mean and standard deviation, the 90% confidence interval is reduced from $\pm 0.001_7$ to $\pm ts/\sqrt{n} = \pm(1.725)(0.001_8)/\sqrt{21} = \pm 0.000\,7$ mL.

Frequently, we use the standard deviation as the estimated uncertainty. For five measurements, we would report a volume of $6.374_6 \pm 0.001_8$ mL. It is good practice to report the number of measurements, so that confidence intervals can be calculated.

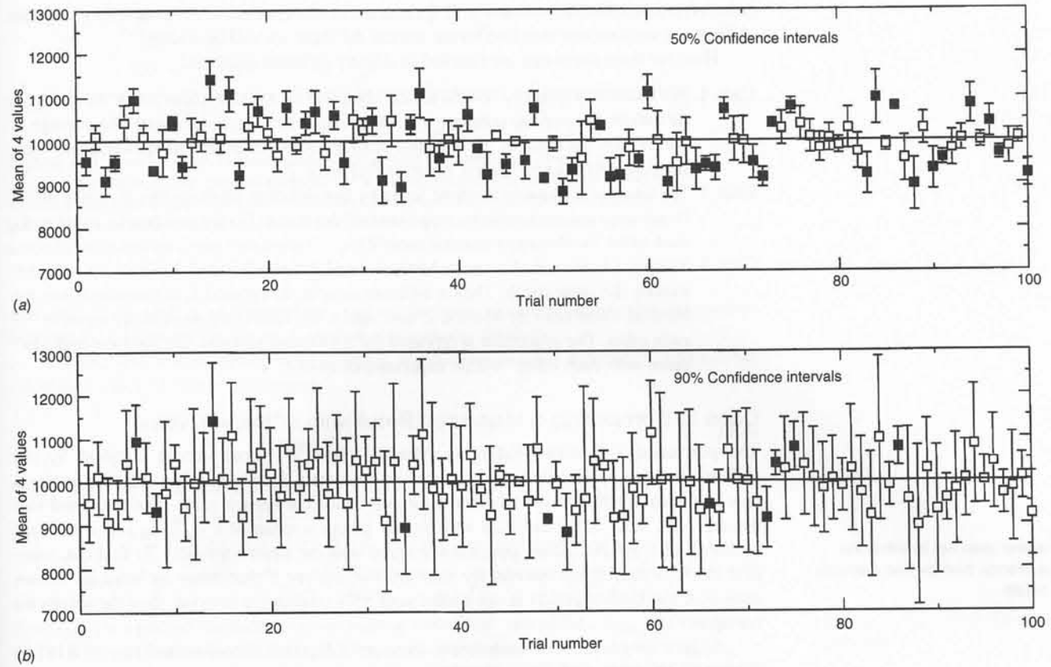


Figure 4-5 50% and 90% confidence intervals for the same set of random data. Filled squares are the data points whose confidence interval does not include the true population mean of 10 000.

The Meaning of a Confidence Interval

Figure 4-5 illustrates the meaning of confidence intervals. A computer chose numbers at random from a Gaussian population with a population mean (μ) of 10 000 and a population standard deviation (σ) of 1 000 in Equation 4-3. In trial 1, four numbers were chosen, and their mean and standard deviation were calculated with Equations 4-1 and 4-2. The 50% confidence interval was then calculated with Equation 4-6, using $t = 0.765$ from Table 4-2 (50% confidence, 3 degrees of freedom). This trial is plotted as the first point at the left in Figure 4-5a; the square is centered at the mean value of 9 526, and the error bar extends from the lower limit to the upper limit of the 50% confidence interval (±290). The experiment was repeated 100 times to produce the points in Figure 4-5a.

The 50% confidence interval is defined such that, if we repeated this experiment an infinite number of times, 50% of the error bars in Figure 4-5a would include the true population mean of 10 000. In fact, I did the experiment 100 times, and 45 of the error bars in Figure 4-5a pass through the horizontal line at 10 000.

Figure 4-5b shows the same experiment with the same set of random numbers, but this time the 90% confidence interval was calculated. For an infinite number of experiments, we would expect 90% of the confidence intervals to include the population mean of 10 000. In Figure 4-5b, 89 of the 100 error bars cross the horizontal line at 10 000.

4-3 Comparison of Means with Student's *t*

We use a ***t* test** to compare one set of measurements with another to decide whether or not they are "the same." Statisticians say we are testing the *null hypothesis,* which states that the mean values from two sets of measurements are *not* different. Because of inevitable random errors, we do not expect the mean values to be exactly the same, even if we are measuring the same physical quantity. Statistics gives us a probability that the observed difference between two means can arise from purely random measurement error. We customarily reject the null hypothesis if there is less than a 5% chance that the observed difference arises from random

Confidence limits and the *t* test (and, later in this chapter, the Q test) assume that data follow a Gaussian distribution. If they do not, different formulas would be required.

For Rayleigh's data in Figure 4-6, we suspect that the population standard deviation from air is smaller than that from chemical sources. Using Equations 4-8a and 4-9a, we find that $t_{calculated} = 21.7$ and degrees of freedom $= 7.22 \approx 7$. This value of $t_{calculated}$ still far exceeds values in Table 4-2 for 7 degrees of freedom at 95% or 99.9% confidence.

Case 3. Paired *t* test for Comparing Individual Differences

In this case, we use two methods to make single measurements on several different samples. No measurement has been duplicated. Do the two methods give the same answer "within experimental error"? Figure 4-7 shows measurements of aluminum in 11 samples of drinking water. Results for Method 1 are in column B and results for Method 2 are in column C. For each sample, the two results are similar, but not identical.

To see if there is a significant difference between the methods, we use the paired *t* test. First, column D computes the difference (d_i) between the two results for each sample. The mean of the 11 differences ($\bar{d} = -2.4_{91}$) is computed in cell D16 and the standard deviation of the 11 differences (s_d) is computed in cell D17.

$$s_d = \sqrt{\frac{\sum (d_i - \bar{d})^2}{n - 1}} \tag{4-10}$$

$$s_d = \sqrt{\frac{(-3.0 - \bar{d})^2 + (4.8 - \bar{d})^2 + \cdots + (0.2 - \bar{d})^2 + (-11.6 - \bar{d})^2}{11 - 1}} = 6.7_{48}$$

Once you have the mean and standard deviation, compute $t_{calculated}$ with the formula

$$t_{calculated} = \frac{|\bar{d}|}{s_d}\sqrt{n} \tag{4-11}$$

where $|\bar{d}|$ is the absolute value of the mean difference, so that $t_{calculated}$ is always positive. Inserting the mean and standard deviation into Equation 4-11 gives

$$t_{calculated} = \frac{2.4_{91}}{6.7_{48}}\sqrt{11} = 1.2_{24}$$

We find that $t_{calculated}$ (1.2_{24}) is less than t_{table} (2.228) listed in Table 4-2 for 95% confidence and 10 degrees of freedom. *There is less than a 95% chance that the two results are different.*

You may appreciate Box 4-1 at this time.

	A	B	C	D
1	Comparison of two methods for measuring Al			
2				
3	Sample	Method 1	Method 2	Difference
4	number	(μg/L)	(μg/L)	(d_i)
5	1	17.2	14.2	−3.0
6	2	23.1	27.9	4.8
7	3	28.5	21.2	−7.3
8	4	15.3	15.9	0.6
9	5	23.1	32.1	9.0
10	6	32.5	22.0	−10.5
11	7	39.5	37.0	−2.5
12	8	38.7	41.5	2.8
13	9	52.5	42.6	−9.9
14	10	42.6	42.8	0.2
15	11	52.7	41.1	−11.6
16			mean =	−2.491
17			std dev =	6.748
18			$t_{calculated}$ =	1.224
19	D5 = C5-B5			
20	D16 = AVERAGE(D5:D15)			
21	D17 = STDEV(D5:D15)			
22	D18 = ABS(D16)*SQRT(A15)/D17			
23		ABS = absolute value		

Figure 4-7 Measurement of Al by 2 methods. *[Data from P. T. Srinivasan, T. Viraraghavan, and K. S. Subramanian, "Method Development for Drinking Water Aluminum Measurement Using a Graphite Furnace Atomic Absorption Spectrophotometer," Am. Lab., February 2000, p. 76.]*

Box 4-1 Analytical Chemistry and the Law

As a person who will either derive or use analytical results, you should be aware of this warning:[3]

> Analytical chemists must always emphasize to the public that *the single most important characteristic of any result obtained from one or more analytical measurements is an adequate statement of its uncertainty interval.* Lawyers usually attempt to dispense with uncertainty and try to obtain unequivocal statements; therefore, an uncertainty interval must be clearly defined in cases involving litigation and/or enforcement proceedings. Otherwise, a value of 1.001 without a specified uncertainty, for example, may be viewed as legally exceeding a permissible level of 1.

Some legal limits make no scientific sense. The Delaney Amendment to the U.S. Federal Food, Drug, and Cosmetic Act of 1958 stated that "no additive [in processed food] shall be deemed to be safe if it is found to induce cancer when ingested by man or animal." This statement meant that no detectable level of any carcinogenic (cancer-causing) pesticide may remain in processed foods, even if the level is far below that which can be shown to cause cancer. The law was passed at a time when the sensitivity of analytical procedures was relatively poor, so the detection limit was relatively high. As sensitivity improved, concentrations of detectable chemical residues decreased by 10^3 to 10^6. A concentration that was acceptable in 1965 was 10^6 times above the legal limit in 1995, regardless of whether there was any evidence that such a low level is harmful. In 1996, Congress changed the law so that the allowed level probably will be set at a concentration that produces less than one excess cancer per million persons exposed. Unfortunately, the scientific basis for predicting effects of low-level exposure on human health is slim.[4]

4-4 Comparison of Standard Deviations with the *F* Test

To decide whether Rayleigh's two sets of nitrogen masses in Figure 4-6 are "significantly" different from each other, we used the *t* test. If the standard deviations of two data sets are not significantly different from each other, then we use Equation 4-8 for the *t* test. If the standard deviations are significantly different, then we use Equation 4-8a instead.

Use the *F* test for Case 2 in comparison of means in Section 4-3.

The ***F* test** tells us whether two standard deviations are "significantly" different from each other. *F* is the quotient of the squares of the standard deviations:

$$F_{calculated} = \frac{s_1^2}{s_2^2} \tag{4-12}$$

If $F_{calculated} > F_{table}$ (95%), the standard deviations are significantly different from each other.
If $F_{calculated} < F_{table}$, use Equation 4-8.
If $F_{calculated} > F_{table}$, use Equation 4-8a.

We always put the larger standard deviation in the numerator so that $F \geq 1$. If $F_{calculated} > F_{table}$ in Table 4-4, then the difference is significant.

The square of the standard deviation is called the *variance*.

Table 4-4 Critical values of $F = s_1^2/s_2^2$ at 95% confidence level

Degrees of freedom for s_2	Degrees of freedom for s_1													
	2	3	4	5	6	7	8	9	10	12	15	20	30	∞
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.5	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.84	8.81	8.79	8.74	8.70	8.66	8.62	8.53
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.75	5.63
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.62	4.56	4.50	4.36
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.81	3.67
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.58	3.51	3.44	3.38	3.23
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.08	2.93
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94	2.86	2.71
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.84	2.77	2.70	2.54
11	3.98	3.59	3.36	3.20	3.10	3.01	2.95	2.90	2.85	2.79	2.72	2.65	2.57	2.40
12	3.88	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.47	2.30
13	3.81	3.41	3.18	3.02	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46	2.38	2.21
14	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.31	2.13
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33	2.25	2.07
16	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.19	2.01
17	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.23	2.15	1.96
18	3.56	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19	2.11	1.92
19	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16	2.07	1.88
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12	2.04	1.84
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.09	2.01	1.93	1.84	1.62
∞	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57	1.46	1.00

Example Are the Two Standard Deviations of Rayleigh's Data Significantly Different from Each Other?

In Table 4-3, the larger standard deviation is $s_1 = 0.001\,38$ ($n_1 = 8$ measurements) and the smaller standard deviation is $s_2 = 0.000\,14_3$ ($n_2 = 7$ measurements).

Solution To answer the question, find F with Equation 4-12:

$$F_{\text{calculated}} = \frac{s_1^2}{s_2^2} = \frac{(0.001\,38)^2}{(0.000\,14_3)^2} = 93._1$$

In Table 4-4, look for F_{table} in the column with 7 degrees of freedom for s_1 (because degrees of freedom $= n - 1$) and the row with 6 degrees of freedom for s_2. *Because $F_{calculated}$ (= 93.1) > F_{table} (= 4.21), the standard deviations are different from each other above the 95% confidence level.* The obvious difference in scatter of the two data sets in Figure 4-6 is highly significant.

4-5 *t* Tests with a Spreadsheet

Excel has built-in procedures for conducting tests with Student's t. To compare Rayleigh's two sets of results in Table 4-3, enter his data in columns B and C of a spreadsheet (Figure 4-8). In rows 13 and 14, we computed the averages and standard deviations, but we did not need to do this.

In the TOOLS menu, you might find DATA ANALYSIS. If not, select ADD-INS in the TOOLS menu and find ANALYSIS TOOLPACK. Put an x beside ANALYSIS TOOLPACK and click OK. DATA ANALYSIS will then be available in the TOOLS menu.

Returning to Figure 4-8, we want to know whether the mean values of the two sets of data are statistically the same or not. In the TOOLS menu, select DATA ANALYSIS. In the window that appears, select t-Test: Two-Sample Assuming Equal Variances. Click OK. The next window asks you in which cells the data are located. Write B5:B12 for Variable 1 and C5:C12 for Variable 2. The routine ignores the blank space in cell B12. For the Hypothesized Mean Difference enter 0 and for Alpha enter 0.05. Alpha is the level of probability to which we are testing the difference in the means. With Alpha = 0.05, we are at the 95% confidence level. For Output Range, select cell E1 and click OK.

	A	B	C	D	E	F	G
1	Analysis of Rayleigh's Data				t-Test: Two-Sample Assuming Equal Variances		
2						*Variable 1*	*Variable 2*
3		Mass of gas (g) collected from			Mean	2.310109	2.299473
4		air	chemical		Variance	2.03E-08	1.9E-06
5		2.31017	2.30143		Observations	7	8
6		2.30986	2.29890		Pooled Variance	1.03E-06	
7		2.31010	2.29816		Hypothesized Mean Diff	0	
8		2.31001	2.30182		df	13	
9		2.31024	2.29869		t Stat	20.21372	
10		2.31010	2.29940		P(T<=t) one-tail	1.66E-11	
11		2.31028	2.29849		t Critical one-tail	1.770932	
12			2.29889		P(T<=t) two-tail	3.32E-11	
13	Average	2.31011	2.29947		t Critical two-tail	2.160368	
14	Std Dev	0.00014	0.00138				
15					t-Test: Two-Sample Assuming Unequal Variances		
16	B13 = AVERAGE(B5:B12)					*Variable 1*	*Variable 2*
17	B14 = STDEV(B5:B12)				Mean	2.310109	2.299473
18					Variance	2.03E-08	1.9E-06
19					Observations	7	8
20					Hypothesized Mean Diff	0	
21					df	7	
22					t Stat	21.68022	
23					P(T<=t) one-tail	5.6E-08	
24					t Critical one-tail	1.894578	
25					P(T<=t) two-tail	1.12E-07	
26					t Critical two-tail	2.364623	

Figure 4-8 Spreadsheet for comparing mean values of Rayleigh's measurements in Table 4-3.

Excel now goes to work and prints results in cells E1 to G13 of Figure 4-8. Mean values are in cells F3 and G3. Cells F4 and G4 give *variance,* which is the square of the standard deviation. Cell F6 gives *pooled variance* computed with Equation 4-9. That equation was painful to use by hand. Cell F8 shows degrees of freedom ($df = 13$) and $t_{\text{calculated}} = 20.2$ from Equation 4-8 appears in cell F9.

At this point in Section 4-3, we consulted Table 4-2 to find that t_{table} lies between 2.228 and 2.131 for 95% confidence and 13 degrees of freedom. Excel gives us the critical value of t (2.160) in cell F13 of Figure 4-8. Because $t_{\text{calculated}}$ (= 20.2) > t_{table} (= 2.160), we conclude that the two means are not the same. The difference is significant. Cell F12 states that the probability of observing these two mean values and standard deviations by random chance if the mean values were really the same is 3.32×10^{-11}. The difference is *highly* significant. For any value of $P \leq 0.05$ in cell F12, we would reject the null hypothesis and conclude that the means are not the same.

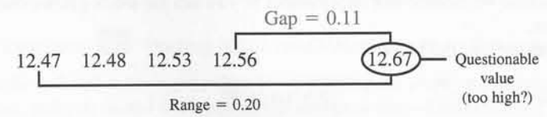
Note 5 for this chapter (in the Notes and References section of the book) explains what is meant by 1-tail and 2-tail in the Excel output in Figure 4-8. We use the 2-tailed test in this book.

The F test in Equation 4-12 told us that the standard deviations of Rayleigh's two experiments are different. Therefore, we can select the other t test found in the TOOLS menu in the DATA ANALYSIS choices. Select t-Test: Two-Sample Assuming Unequal Variances and fill in the blanks exactly as before. Results based on Equations 4-8a and 4-9a are displayed in cells E15 to G26 of Figure 4-8. Just as we found in Section 4-3, the degrees of freedom are $df = 7$ (cell F21) and $t_{\text{calculated}} = 21.7$ (cell F22). Because $t_{\text{calculated}}$ is greater than the critical value of t (2.36 in cell F26), we reject the null hypothesis and conclude that the two means *are* significantly different.

4-6 Q Test for Bad Data

Sometimes one datum is inconsistent with the remaining data. You can use the ***Q* test** to help decide whether to retain or discard a questionable datum. Consider the five results 12.53, 12.56, 12.47, 12.67, and 12.48. Is 12.67 a "bad point"? To apply the Q test, arrange the data in order of increasing value and calculate Q, defined as

$$Q_{\text{calculated}} = \frac{\text{gap}}{\text{range}} \qquad \textbf{(4-13)}$$



The *range* is the total spread of the data. The *gap* is the difference between the questionable point and the nearest value.

If $Q_{\text{calculated}} > Q_{\text{table}}$, the questionable point should be discarded. In the preceding example, $Q_{\text{calculated}} = 0.11/0.20 = 0.55$. In Table 4-5, we find $Q_{\text{table}} = 0.64$. *Because $Q_{calculated} < Q_{table}$, the questionable point should be retained.* There is more than a 10% chance that the value 12.67 is a member of the same population as the other four numbers.

Some people would argue that you should never discard a datum unless you know that there was an error in the procedure that led to that particular measurement. Others would repeat the questionable measurement several more times to gain higher confidence that one measurement is really out of line (or not). The decision is yours and it is subjective.

Table 4-5 is based on 90% confidence. If $Q_{\text{calculated}} > Q_{\text{table}}$, discard the questionable point.

Table 4-5 Values of *Q* for rejection of data

Q (90% confidence)[a]	Number of observations
0.76	4
0.64	5
0.56	6
0.51	7
0.47	8
0.44	9
0.41	10

a. Q = gap/range. If $Q_{calculated} > Q_{table}$, the value in question can be rejected with 90% confidence.

SOURCE: R. B. Dean and W. J. Dixon, Anal. Chem. ***1951,*** *23, 636; see also D. R. Rorabacher, Anal. Chem.* ***1991,*** *63, 139.*

4-7 The Method of Least Squares

For most chemical analyses, the response of the procedure must be evaluated for known quantities of analyte (called *standards*) so that the response to an unknown quantity can be interpreted. For this purpose, we commonly prepare a **calibration curve,** such as the one for caffeine in Figure 0-7. Most often, we work in a region where the calibration curve is a straight line.

We use the **method of least squares** to draw the "best" straight line through experimental data points that have some scatter and do not lie perfectly on a straight line.[6] The best line will be such that some of the points lie above and some lie below the line. We will learn to

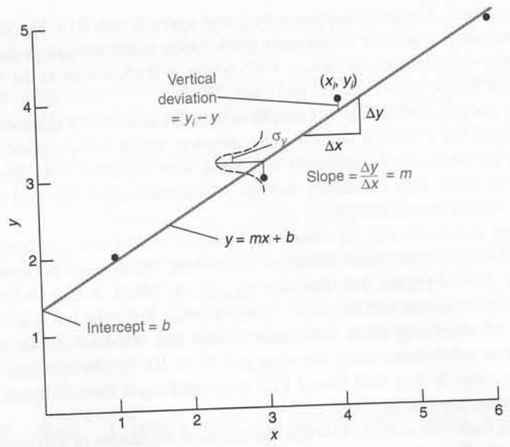


Figure 4-9 Least-squares curve fitting. The points (1,2) and (6,5) do not fall exactly on the solid line, but they are too close to the line to show their deviations. The Gaussian curve drawn over the point (3,3) is a schematic indication of the fact that each value of y_i is normally distributed about the straight line. That is, the most probable value of y will fall on the line, but there is a finite probability of measuring y some distance from the line.

estimate the uncertainty in a chemical analysis from the uncertainties in the calibration curve and in the measured response to replicate samples of unknown.

Finding the Equation of the Line

The procedure we use assumes that the errors in the y values are substantially greater than the errors in the x values.[7] This condition is usually true in a calibration curve in which the experimental response (y values) is less certain than the quantity of analyte (x values). A second assumption is that uncertainties (standard deviations) in all the y values are similar.

Suppose we seek to draw the best straight line through the points in Figure 4-9 by minimizing the vertical deviations between the points and the line. We minimize only the vertical deviations because we assume that uncertainties in y values are much greater than uncertainties in x values.

Let the equation of the line be

Equation of straight line: $y = mx + b$ (4-14)

in which m is the **slope** and b is the **y-intercept.** The vertical deviation for the point (x_i, y_i) in Figure 4-9 is $y_i - y$, where y is the ordinate of the straight line when $x = x_i$.

$$\text{Vertical deviation} = d_i = y_i - y = y_i - (mx_i + b) \tag{4-15}$$

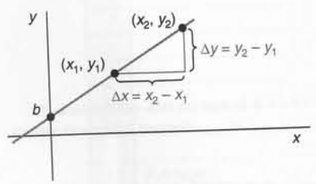
Some of the deviations are positive and some are negative. Because we wish to minimize the magnitude of the deviations irrespective of their signs, we square all the deviations so that we are dealing only with positive numbers:

$$d_i^2 = (y_i - y)^2 = (y_i - mx_i - b)^2$$

Because we minimize the squares of the deviations, this is called the *method of least squares.* It can be shown that minimizing the squares of the deviations (rather than simply their magnitudes) corresponds to assuming that the set of y values is the most probable set.

Finding values of m and b that minimize the sum of the squares of the vertical deviations involves some calculus, which we omit. We will express the final solution for slope and intercept in terms of *determinants,* which summarize certain arithmetic operations. The **determinant** $\begin{vmatrix} e & f \\ g & h \end{vmatrix}$ represents the value $eh - fg$. So, for example,

$$\begin{vmatrix} 6 & 5 \\ 4 & 3 \end{vmatrix} = (6 \times 3) - (5 \times 4) = -2$$



Equation for a straight line: $y = mx + b$

Slope (m) $= \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$

y-intercept (b) = crossing point on y-axis

To evaluate the determinant, multiply the diagonal elements $e \times h$ and then subtract the product of the other diagonal elements $f \times g$.

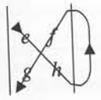


Table 4-6 Calculations for least-squares analysis

x_i	y_i	$x_i y_i$	x_i^2	$d_i (= y_i - mx_i - b)$	d_i^2
1	2	2	1	0.038 46	0.001 479 3
3	3	9	9	−0.192 31	0.036 982
4	4	16	16	0.192 31	0.036 982
6	5	30	36	−0.038 46	0.001 479 3
$\Sigma x_i = 14$	$\Sigma y_i = 14$	$\Sigma(x_i y_i) = 57$	$\Sigma(x_i^2) = 62$		$\Sigma(d_i^2) = 0.076\,923$

The slope and the intercept of the "best" straight line are found to be

$$\text{Least-squares "best" line} \begin{cases} \text{Slope:} & m = \begin{vmatrix} \Sigma(x_i y_i) & \Sigma x_i \\ \Sigma y_i & n \end{vmatrix} \div D & (4\text{-}16) \\ \text{Intercept:} & b = \begin{vmatrix} \Sigma(x_i^2) & \Sigma(x_i y_i) \\ \Sigma x_i & \Sigma y_i \end{vmatrix} \div D & (4\text{-}17) \end{cases}$$

Translation of least-squares equations:

$$m = \frac{n\Sigma(x_i y_i) - \Sigma x_i \Sigma y_i}{n\Sigma(x_i^2) - (\Sigma x_i)^2}$$

$$b = \frac{\Sigma(x_i^2)\Sigma y_i - (\Sigma x_i y_i)\Sigma x_i}{n\Sigma(x_i^2) - (\Sigma x_i)^2}$$

where D is

$$D = \begin{vmatrix} \Sigma(x_i^2) & \Sigma x_i \\ \Sigma x_i & n \end{vmatrix} \tag{4-18}$$

and n is the number of points.

Let's use these equations to find the slope and intercept of the best straight line through the four points in Figure 4-9. The work is set out in Table 4-6. Noting that $n = 4$ and putting the various sums into the determinants in Equations 4-16, 4-17, and 4-18 gives

$$m = \begin{vmatrix} 57 & 14 \\ 14 & 4 \end{vmatrix} \div \begin{vmatrix} 62 & 14 \\ 14 & 4 \end{vmatrix} = \frac{(57 \times 4) - (14 \times 14)}{(62 \times 4) - (14 \times 14)} = \frac{32}{52} = 0.615\,38$$

$$b = \begin{vmatrix} 62 & 57 \\ 14 & 14 \end{vmatrix} \div \begin{vmatrix} 62 & 14 \\ 14 & 4 \end{vmatrix} = \frac{(62 \times 14) - (57 \times 14)}{(62 \times 4) - (14 \times 14)} = \frac{70}{52} = 1.346\,15$$

The equation of the best straight line through the points in Figure 4-9 is therefore

$$y = 0.615\,38x + 1.346\,15$$

We tackle the question of significant figures for m and b in the next section.

Example Finding Slope and Intercept with a Spreadsheet

Your scientific calculator has a procedure for computing the slope and intercept of a set of (x,y) data, and you should learn how to use that procedure. Alternatively, Excel has functions called SLOPE and INTERCEPT whose use is illustrated here:

	A	B	C	D	E	F
1	x	y			Formulas:	
2	1	2		slope =		
3	3	3		0.61538	D3 = SLOPE(B2:B5,A2:A5)	
4	4	4		intercept =		
5	6	5		1.34615	D5 = INTERCEPT(B2:B5,A2:A5)	

The slope in cell D3 is computed with the formula "= SLOPE(B2:B5,A2:A5)", where B2:B5 is the range containing the y values and A2:A5 is the range containing x values.

How Reliable Are Least-Squares Parameters?

To estimate the uncertainties (expressed as standard deviations) in the slope and intercept, an uncertainty analysis must be performed on Equations 4-16 and 4-17. Because the uncertainties in m and b are related to the uncertainty in measuring each value of y, we first estimate the standard deviation that describes the population of y values. This standard deviation, σ_y, characterizes the little Gaussian curve inscribed in Figure 4-9.

We estimate σ_y, the population standard deviation of all y values, by calculating s_y, the standard deviation, for the four measured values of y. The deviation of each value of y_i from