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The Chemistry of Volumetric and Gravimetric Analysis (Theory)

(CHEM211)

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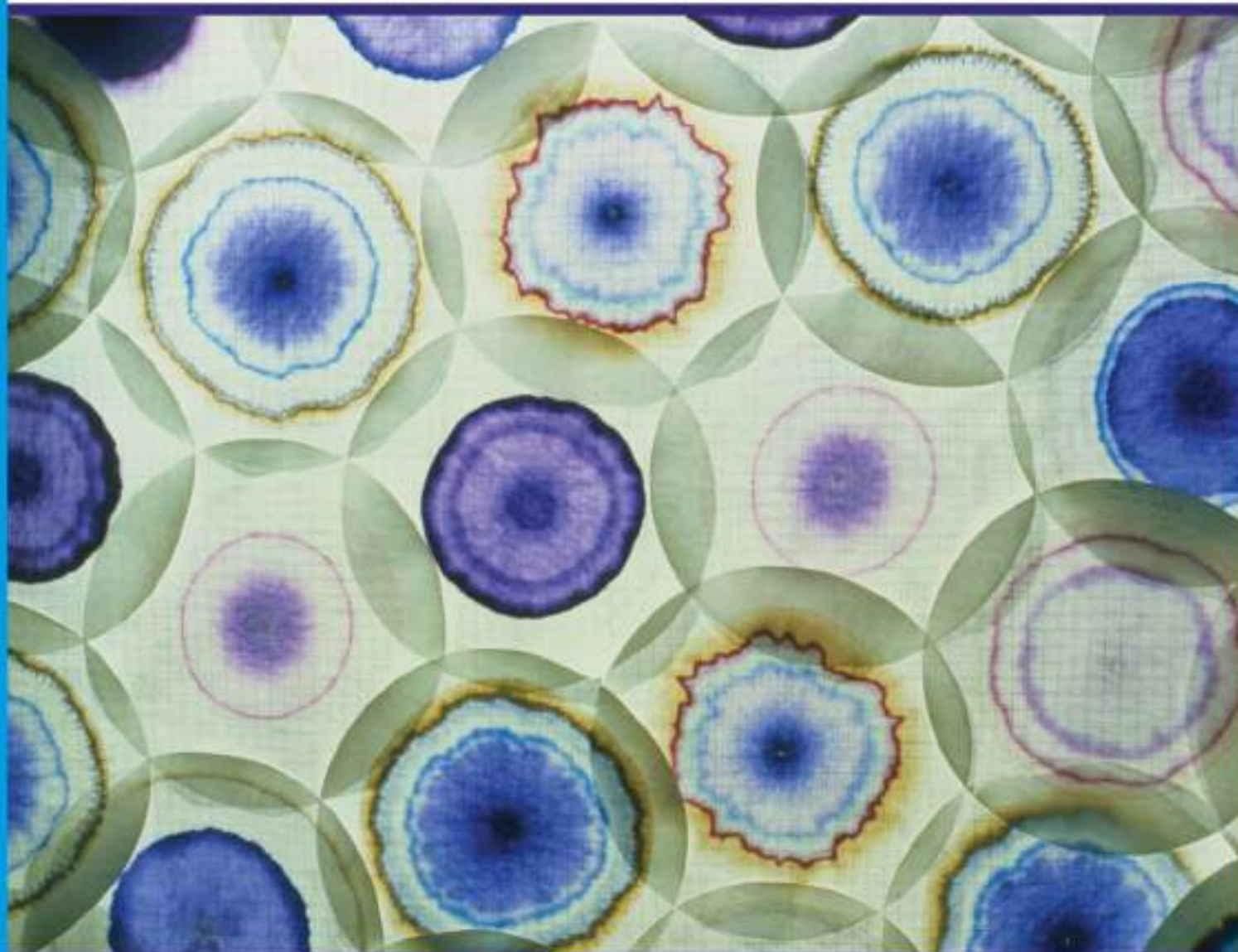
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Fundamentals of
**ANALYTICAL
CHEMISTRY** 10E



F. James Holler | Stanley R. Crouch

Fundamentals of Analytical Chemistry

Tenth Edition

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CHAPTER ONE

**Introduction to Analytical Chemistry and
Chemical Analysis**

The Nature of Analytical Chemistry

Analytical chemistry is a measurement science consisting of a set of powerful ideas and methods that are useful in all fields of science, engineering, and medicine. Some exciting illustrations of the power and significance of analytical chemistry have occurred, are occurring, and will occur during NASA's rover explorations of the planet Mars. On July 4, 1997, the Pathfinder spacecraft delivered the Sojourner rover to the Martian surface. Analytical instruments returned information on the chemical composition of rocks and soil. Investigations by the lander and rover suggested that Mars was at one time in its past warm and wet with liquid water on the surface and water vapor in the atmosphere. In January 2004, the Mars rovers Spirit and Opportunity arrived on Mars for a 3-month mission. A major result from Spirit's alpha particle X-ray spectrometer (APXS) and Mossbauer spectrometer was finding concentrated deposits of silica and, at a different site, high concentrations of carbonate. Spirit continued to explore and transmit data until 2010, outliving even the most optimistic predictions. Even more amazing, Opportunity continued to travel the surface of Mars and, by March, 2012, had covered more than 21 miles exploring and transmitting images of craters, small hills, and other features.

In late 2011, the Mars Science Laboratory aboard the rover Curiosity was launched. It arrived on August 6, 2012, with a host of analytical instruments on board. The Chemistry and Camera package includes a laser-induced breakdown spectrometer (LIBS, see Chapter 26) and a remote microimager. The LIBS instrument will provide determination of many elements with no sample preparation. It can determine the identity and amounts of major, minor, and trace elements and can detect hydrated minerals. The sample analysis package contains a quadrupole mass spectrometer (Chapter 27), a gas chromatograph (Chapter 30), and a tunable laser spectrometer (Chapter 23). Its goals are to survey carbon compound sources, search for organic compounds important to life, reveal the chemical and



Perseverance Rover using drill and robotic arm to collect samples.

NASA/JPL-Caltech

isotopic states of several elements, determine the composition of the Martian atmosphere, and search for noble gas and light element isotopes.¹

At the end of July 2020, the Mars 2020 Rover mission was launched. The Perseverance Rover that is part of this mission will focus on questions concerning the potential for life on Mars. It will seek signs of conditions on Mars in the past that indicate the presence of life. Core samples taken by the rover drill will be collected and stored for possible return to Earth for analysis in the future. The mission will also obtain information relevant to future human Mars explorations including possible habitation of the planet. It will explore producing oxygen from the Martian atmosphere, finding subsurface water, and characterizing Martian weather and other environmental conditions that could influence living and working on the planet. Perseverance successfully landed on Mars on February 18, 2021.

Qualitative analysis reveals the *identity* of the elements and compounds in a sample.

Quantitative analysis indicates the *amount* of each substance in a sample.

Analytes are the components of a sample that are determined.

These examples demonstrate that both qualitative and quantitative information are required in an analysis. **Qualitative analysis** establishes the chemical identity of the species in the sample. **Quantitative analysis** determines the relative amounts of these species, or **analytes**, in numerical terms. The data from the various spectrometers on the rovers contain both types of information. As is common with many analytical instruments, the gas chromatograph and mass spectrometer incorporate a separation step as a necessary part of the analytical process. With a few analytical tools, exemplified here by the APXS and LIBS experiments, chemical separation of the various elements contained in the rocks is unnecessary since the methods provide highly selective information. This text explores quantitative methods of analysis, separation methods, and the principles behind their operation. A qualitative analysis is often an integral part of the separation step, and determining the identity of the analytes is an essential adjunct to quantitative analysis.

1A The Role of Analytical Chemistry

Analytical chemistry is applied throughout industry, medicine, and all the sciences. To illustrate, consider a few examples. The concentrations of oxygen and of carbon dioxide are determined in millions of blood samples every day and used to diagnose and treat illnesses. Quantities of hydrocarbons, nitrogen oxides, and carbon monoxide present in automobile exhaust gases are measured to determine the effectiveness of emission-control devices. Quantitative measurements of ionized calcium in blood serum help diagnose parathyroid disease in humans. Quantitative determination of nitrogen in foods establishes their protein content and thus their nutritional value. Analysis of steel during its production permits adjustment in the concentrations of such elements as carbon, nickel, and chromium to achieve a desired strength, hardness, corrosion resistance, and ductility. The mercaptan content of household gas supplies is monitored continually to ensure that the gas has a sufficiently obnoxious odor to warn of dangerous leaks. Farmers tailor fertilization and irrigation schedules to meet changing plant needs during the growing season, gauging these needs from quantitative analyses of plants and soil.

Quantitative analytical measurements also play a vital role in many research areas in chemistry, biochemistry, biology, geology, physics, and the other sciences. For example, quantitative measurements of potassium, calcium, and sodium ions

¹For details on the Mars Science missions and the rovers Curiosity, see <http://www.nasa.gov>.

in the body fluids of animals permit physiologists to study the role these ions play in nerve-signal conduction as well as muscle contraction and relaxation. Chemists unravel the mechanisms of chemical reactions through reaction rate studies. The rate of consumption of reactants or formation of products in a chemical reaction can be calculated from quantitative measurements made at precise time intervals. Materials scientists rely heavily on quantitative analyses of crystalline germanium and silicon in their studies of semiconductor devices whose impurities lie in the concentration range of 1×10^{-6} to 1×10^{-9} percent. Archaeologists identify the sources of volcanic glasses (obsidian) by measuring concentrations of minor elements in samples taken from various locations. This knowledge in turn makes it possible to trace prehistoric trade routes for tools and weapons fashioned from obsidian.

Many chemists, biochemists, and medicinal chemists devote much time in the laboratory gathering quantitative information about systems that are important and interesting to them. The central role of analytical chemistry in this enterprise and many others is illustrated in Figure 1-1. All branches of chemistry draw on the ideas and techniques of analytical chemistry. Analytical chemistry has a similar function



FIGURE 1-1

The relationship between analytical chemistry, other branches of chemistry, and the other sciences. The central location of analytical chemistry in the diagram signifies its importance and the breadth of its interactions with many other disciplines.

with respect to the many other scientific fields listed in the diagram. Chemistry is often called *the central science*; its top-center position and the central position of analytical chemistry in the figure emphasize this importance. The interdisciplinary nature of chemical analysis makes it a vital tool in medical, industrial, government, and academic laboratories throughout the world.

1B Quantitative Analytical Methods

We compute the results of a typical quantitative analysis from two measurements. One is the mass or the volume of sample being analyzed. The second measurement is of some quantity that is proportional to the amount of analyte in the sample such as mass, volume, intensity of light, or electrical charge. This second measurement usually completes the analysis, and we usually classify analytical methods according to the nature of this final measurement. **Gravimetric methods** determine the mass of the analyte or some compound chemically related to it. A **volumetric method** measures the volume of a solution containing sufficient reagent to react completely with the analyte. **Electroanalytical methods** measure electrical properties such as potential, current, resistance, and quantity of electrical charge. **Spectroscopic methods** explore the interaction between electromagnetic radiation and analyte atoms or molecules or the emission of radiation by analytes. Finally, in a group of miscellaneous methods, we measure such quantities as mass-to-charge ratio of ions by mass spectrometry, rate of radioactive decay, heat of reaction, rate of reaction, sample thermal conductivity, optical activity, and refractive index.



EPA (Environmental Protection Agency)

Dr. Ann Richard completed her Ph.D. at the University of North Carolina at Chapel Hill, specializing in physical chemistry. Using her computational chemistry skill set, she accepted a postdoctoral position at the U.S. Environmental Protection Agency (EPA), where she has worked since 1984. Dr. Richard is currently a researcher for the EPA's Center for Computational Toxicology and Exposure where one of her roles is to use computer models to predict the toxicity of molecules toward both humans and animals. She also combines chemistry, computer science, and data management in the area known as cheminformatics. Dr. Richard manages a large toxicity database and oversees a toxicity testing system utilizing testing plates the size of an iPhone. This system can analyze over 1,500 chemical compounds at one time. Computational toxicology has changed testing procedures, reducing testing of these compounds on animals.

1C A Typical Quantitative Analysis

A typical quantitative analysis includes the sequence of steps shown in the flow diagram of **Figure 1-2**. In some instances, one or more of these steps can be omitted. For example, if the sample is already a liquid, we can avoid the dissolution step. Chapters 1 through 32 focus on the last three steps in **Figure 1-2**. In the measurement step, we measure one of the physical properties mentioned in Section 1B. In the calculation step, we find the relative amount of the analyte present in the samples. In the final step, we evaluate the quality of the results and estimate their reliability.

In the paragraphs that follow, you will find a brief overview of each of the nine steps shown in **Figure 1-2**. We then present a case study to illustrate the use of these steps in solving an important and practical analytical problem. The details of this study foreshadow many of the methods and ideas you will explore as you study analytical chemistry.

1C-1 Choosing a Method

The essential first step in any quantitative analysis is the selection of a method as depicted in **Figure 1-2**. The choice is sometimes difficult and requires experience as well as intuition. One of the first questions that must be considered in the selection process is the level of accuracy required. Unfortunately, high reliability nearly always requires a large investment of time. The selected method usually represents a compromise between the accuracy required and the time and money available for the analysis.

A second consideration related to economic factors is the number of samples that will be analyzed. If there are many samples, we can afford to spend a significant

The case study of Feature 1-1 illustrates how chemical analysis is used in the identification and determination of quantities of hazardous chemicals in the environment. Many of the methods and instruments of analytical chemistry are used routinely to provide vital information in environmental and toxicological studies of this type. The system flow diagram of Figure 1-3 may be applied to this case study. The desired state is a concentration of arsenic that is below the toxic level. Chemical analysis is used to determine the actual state, or the concentration of arsenic in the environment, and this value is compared to the desired concentration. The difference is then used to determine appropriate actions (such as decreased use of arsenical pesticides) to ensure that deer are not poisoned by excessive amounts of arsenic in the environment, which in this example is the controlled system. Many other examples are given in the text and in features throughout this book.

Chapter 1 Summary

- The nature of analytical chemistry
- Quantitative and qualitative analysis
- Analytical chemistry and other branches of science
- Quantitative methods
 - Steps in a typical quantitative analysis
 - Sample preparation
 - Interferences in quantitative methods
 - Calibration
 - Calculation of final results
 - Analytical chemistry as a step in a feedback system
 - Deer kill case study

Key Terms

Analyte, p. 2

Assay, p. 6

Calibration, p. 8

Calibration curve, p. 11

Dry ashing, p. 10

Electroanalytical method, p. 4

Feedback loop, p. 9

Feedback system, p. 9

Flux, p. 7

Fusion, p. 7

Gravimetric method, p. 4

Interferent, p. 7

Matrix, p. 8

Replicate samples, p. 7

Sampling, p. 6

Spectroscopic method, p. 4

Volumetric method, p. 4

Important Equations

$$c_A = kX$$



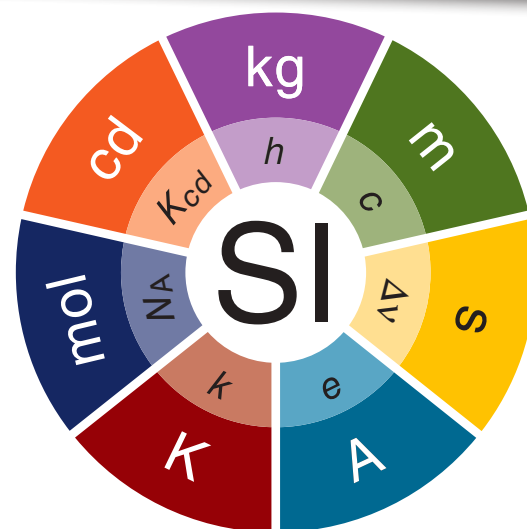
CHAPTER TWO

Basic Chemical Measurements, Units, and Concentrations

Calculations Used in Analytical Chemistry

The International System of Units (Système International [SI]) is based on the seven base units shown here and defined in Table 2-1. It is the modern version of the metric system. Since the meter (m) was redefined in terms of the speed of light in 1960, only the kilogram (kg) was defined as an artifact (mass of a platinum-iridium cylinder) stored in a French vault. Several of the SI base units, including the kilogram, were redefined in 2019 as discussed in this chapter.

The outer circle shows the SI base units (mol = mole, cd = candela, kg = kilogram, m = meter, s = second, A = ampere, K = kelvin). The inner circle shows the base constants on which the units are dependent (N_A = Avogadro's constant, K_{cd} = luminous efficacy, h = Planck's constant, c = speed of light, $\Delta\nu$ = transition frequency of Cs-133 atom, e = electric charge, k = Boltzmann's constant).



In this chapter, we describe several methods used to compute the results of a quantitative analysis. We first present the SI system of units and the distinction between mass and weight. We then discuss the mole, a measure of the amount of a chemical substance. Next, we consider the various ways that concentrations of solutions are expressed. Finally, we treat chemical stoichiometry. You may have studied much of the material in this chapter in your general chemistry courses.

2A Some Important Units of Measurement

2A-1 SI Units

Scientists throughout the world have adopted a standardized system of units known as the **International System of Units (SI)**. This system is based on the seven fundamental base units shown in Table 2-1. Numerous other useful units, such as volts, hertz, coulombs, and joules, are derived from these base units. In 2019, four of the seven SI base units, the kilogram, the ampere, the kelvin, and the mole, were redefined by setting exact values for Planck's constant, h , the elementary electric charge, e , Boltzmann's constant, k , and Avogadro's constant, N_A respectively. The correspondence between the units and the constants used to define them is shown by the inner and outer rings of the pie chart. The new definitions were intended to improve the SI system without significantly changing the values of any of the units. Unchanged numerical values considered constants of nature are the speed of light,

SI is the initialism for the French "Système International d'Unités."

The *angstrom unit* \AA is a non-SI unit of length that is widely used to express the wavelength of very short radiation such as X-rays ($1 \text{\AA} = 0.1 \text{ nm} = 10^{-10} \text{ m}$). Thus, typical X-radiation lies in the range of 0.1 to 10\AA .

TABLE 2-1

SI Base Units		
Physical Quantity	Name of Unit	Abbreviation
Mass	kilogram	kg
Length	meter	m
Time	second	s
Temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	A
Luminous intensity	candela	cd

Kyodo News/Getty Images



For more than a century, the kilogram has been defined as the mass of a single platinum-iridium standard housed in a laboratory in Sèvres, France. Unfortunately, the mass of this “standard” kilogram is subject to drifts, measurement errors, and other uncertainties. The 2019 redefinition of the kilogram defines it in terms of the equivalent mass (m) of the energy ($h\nu$) of a photon, given its exact frequency (ν) and Planck’s constant (h) from

$$E = mc^2 \quad m = \frac{E}{c^2} = \frac{h\nu}{c^2}$$

In the 2019 redefinition, Planck’s constant, the speed of light, and the frequency of the hyperfine transition of the Cs-133 atom were defined as exact quantities, leading to a stable definition of the kilogram in terms of base quantities. While these changes solidify the foundation of SI units in unprecedented fashion, they are so small as to have little influence on practical analytical results.

the hyperfine transition frequency of a Cs-133 atom (frequency in Hz of specific Cs atomic transition), and the luminous efficacy (ratio of luminous flux in lumens to power in watts) of monochromatic green light.

To express small or large measured quantities in terms of a few simple digits, prefixes are used with these base units and other derived units. As shown in Table 2-2, these prefixes multiply the unit by various powers of 10. For example, the wavelength of yellow radiation used for determining sodium by flame photometry is about 5.9×10^{-7} m, which can be expressed more compactly as 590 nm (nanometers); the volume of a liquid injected onto a chromatographic column is often roughly 50×10^{-6} L, or 50 μ L (microliters); or the amount of memory on some computer hard disks is about 20×10^9 bytes, or 20 Gbytes (gigabytes).

In analytical chemistry, we often determine the amount of chemical species from mass measurements. For such measurements, metric units of kilograms (kg), grams (g), milligrams (mg), or micrograms (μ g) are used. Volumes of liquids are measured in units of liters (L), milliliters (mL), microliters (μ L), and sometimes nanoliters (nL). The liter, the SI unit of volume, is a derived unit and not an SI base unit. The liter is defined as exactly 10^{-3} m³. The milliliter is defined as 10^{-6} m³, or 1 cm³.

TABLE 2-2

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

2A-2 The Distinction Between Mass and Weight

It is important to understand the difference between mass and weight. **Mass** is an unchanging measure of the quantity of matter in an object. **Weight** is the force of attraction between an object and its surroundings, principally Earth. Because gravitational attraction varies with geographical location, the weight of an object depends on where you weigh it. For example, a crucible *weighs* less in Denver than in Atlantic City (both cities are at approximately the same latitude) because the attractive force between the crucible and Earth is smaller at the higher altitude of Denver. Similarly, the crucible *weighs* more in Seattle than in Panama (both cities are at sea level) because Earth is somewhat flattened at the poles, and the force of attraction increases measurably with latitude. The *mass* of the crucible, however, remains constant regardless of where you measure it.

Weight and mass are related by the familiar expression

$$w = mg$$

where w is the weight of an object, m is its mass, and g is the acceleration due to gravity.

A chemical analysis is always based on mass so that the results will not depend on locality. A balance is used to compare the mass of an object with the mass of one or more standard masses. Because g affects both unknown and known equally, the mass of the object is identical to the standard masses with which it is compared.

The distinction between mass and weight is often lost in common usage, and the process of comparing masses is usually called *weighing*. In addition, the objects of known mass as well as the results of weighing are frequently called *weights*. Always bear in mind, however, that analytical data are based on mass rather than weight. Therefore, throughout this text, we use mass rather than weight to describe the quantities of substances or objects. On the other hand, for lack of a better word, we use *weigh* for the act of determining the mass of an object. Also, we often say *weights* to mean the standard masses used in weighing.

2A-3 The Mole

The **mole** (abbreviated mol) is the SI unit for the amount of a chemical substance. It is always associated with specific microscopic entities such as atoms, molecules, ions, electrons, other particles, or specified groups of such particles as represented by a chemical formula. One mole contains exactly $6.02214076 \times 10^{23}$ elementary entities (atoms, molecules, ions, electrons, and so on). The fixed number $6.02214076 \times 10^{23}$ is known as Avogadro's constant. When expressed in the unit mol^{-1} , this number is called Avogadro's number, which is often rounded to 6.022×10^{23} . The **molar mass** \mathcal{M} of a substance is the mass in grams of 1 mole of that substance. We calculate molar masses by summing the atomic masses of all the atoms appearing in a chemical formula. For example, the molar mass of formaldehyde CH_2O is

$$\begin{aligned} \mathcal{M}_{\text{CH}_2\text{O}} &= \frac{1 \text{ mol C}}{\text{mol CH}_2\text{O}} \times \frac{12.0 \text{ g}}{\text{mol C}} + \frac{2 \text{ mol H}}{\text{mol CH}_2\text{O}} \times \frac{1.0 \text{ g}}{\text{mol H}} \\ &\quad + \frac{1 \text{ mol O}}{\text{mol CH}_2\text{O}} \times \frac{16.0 \text{ g}}{\text{mol O}} \\ &= 30.0 \text{ g/mol CH}_2\text{O} \end{aligned}$$

Mass m is an unchanging measure of the quantity of matter. **Weight** w is the force of gravitational attraction between that matter and Earth.



Photo of Edwin "Buzz" Aldrin taken by Neil Armstrong in July 1969. Armstrong's reflection may be seen in Aldrin's visor. The suits worn by Armstrong and Aldrin during the Apollo 11 mission to the Moon in 1969 appear to be massive. But because the mass of the Moon is only 1/81 that of Earth and the acceleration due to gravity is only 1/6 that on Earth, the weight of the suits on the Moon was only 1/6 of their weight on Earth. The mass of the suits, however, was identical in both locations.



A **mole** of a chemical species is 6.022×10^{23} atoms, molecules, ions, electrons, ion pairs, or subatomic particles.

and that of glucose, $C_6H_{12}O_6$, is

$$\begin{aligned} \mathcal{M}_{C_6H_{12}O_6} &= \frac{6 \text{ mol C}}{\text{mol } C_6H_{12}O_6} \times \frac{12.0 \text{ g}}{\text{mol C}} + \frac{12 \text{ mol H}}{\text{mol } C_6H_{12}O_6} \times \frac{1.0 \text{ g}}{\text{mol H}} \\ &+ \frac{6 \text{ mol O}}{\text{mol } C_6H_{12}O_6} \times \frac{16.0 \text{ g}}{\text{mol O}} = 180.0 \text{ g/mol } C_6H_{12}O_6 \end{aligned}$$

Thus, 1 mole of formaldehyde has a mass of 30.0 g, and 1 mole of glucose has a mass of 180.0 g.

The number of moles n_X of a species X of molar mass \mathcal{M}_X is given by

$$\text{amount X} = n_X = \frac{m_X}{\mathcal{M}_X}$$

The units work out to

$$\begin{aligned} \text{mol X} &= \frac{\text{g X}}{\text{g X/mol X}} \\ &= \text{g X} \times \frac{\text{mol X}}{\text{g X}} \end{aligned}$$

The number of millimoles (mmol) is given by

$$\begin{aligned} \text{mmol X} &= \frac{\text{g X}}{\text{g X/mmol X}} \\ &= \text{g X} \times \frac{\text{mmol X}}{\text{g X}} \end{aligned}$$

When you make calculations of this kind, you should include all units as we do throughout this chapter. This practice often reveals errors in setting up equations.

FEATURE 2-1

Unified Atomic Mass Units and the Mole

The masses for the elements listed in the table inside the back cover of this text are *relative masses* in terms of *unified atomic mass units* (u) or *daltons* (Da). The dalton is defined as 1/12 the mass of a neutral ^{12}C atom. With the redefinition of SI base units in 2019, the definition of the dalton remained the same. However, the definition of the mole and the kilogram changed in such a way that the molar mass unit is no longer exactly 1 g/mol. In other words, the mass in grams of any substance in 1 mole of that substance is no longer exactly equal to the number of daltons in its average molecular mass. The molar mass of a compound today is the mass of Avogadro's number of molecules of that compound. For most applications in analytical chemistry, the changes are so small as to have little or no influence on results.



Charles D. Winters

Approximately 1 mole of each of several different elements. From left to right are 64 g of copper beads, 18 g of water, 58 g of table salt, 342 g of sucrose (sugar cubes), and 27 g of crumpled aluminum foil.

2A-4 The Millimole

1 mmol = 10^{-3} mol, and
10³ mmol = 1 mol

Sometimes it is more convenient to make calculations with millimoles (mmol) rather than moles. The millimole is 1/1000 of a mole, and the mass in grams of a millimole, the millimolar mass ($m\mathcal{M}$), is likewise 1/1000 of the molar mass.

2A-5 Calculating the Amount of a Substance in Moles or Millimoles

The two examples that follow illustrate how the number of moles or millimoles of a species can be determined from its mass in grams or from the mass of a chemically related species.

EXAMPLE 2-1

Find the number of moles and millimoles of benzoic acid ($M = 122.1 \text{ g/mol}$) that are contained in 2.00 g of the pure acid.

Solution

If we use HBz to represent benzoic acid, we can write that 1 mole of HBz has a mass of 122.1 g. Therefore,

$$\begin{aligned} \text{amount HBz} = n_{\text{HBz}} &= 2.00 \text{ g HBz} \times \frac{1 \text{ mol HBz}}{122.1 \text{ g HBz}} & (2-1) \\ &= 0.0164 \text{ mol HBz} \end{aligned}$$

To obtain the number of millimoles, divide by the millimolar mass (0.1221 g/mmol), that is,

$$\text{amount HBz} = 2.00 \text{ g HBz} \times \frac{1 \text{ mmol HBz}}{0.1221 \text{ g HBz}} = 16.4 \text{ mmol HBz}$$



Molecular model of benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$. Benzoic acid occurs widely in nature, particularly in berries. It finds broad use as a preservative in foods, fats, and fruit juices; as a mordant for dyeing fabric; and as a standard in calorimetry and in acid/base analysis.

EXAMPLE 2-2

What is the mass in grams of Na^+ (22.99 g/mol) in 25.0 g of Na_2SO_4 (142.0 g/mol)?

Solution

The chemical formula indicates that 1 mole of Na_2SO_4 contains 2 moles of Na^+ , that is,

$$\text{amount Na}^+ = n_{\text{Na}^+} = \frac{\text{mol Na}_2\text{SO}_4}{\text{mol Na}_2\text{SO}_4} \times \frac{2 \text{ mol Na}^+}{\text{mol Na}_2\text{SO}_4}$$

To find the number of moles of Na_2SO_4 , proceed as in Example 2-1:

$$\text{amount Na}_2\text{SO}_4 = n_{\text{Na}_2\text{SO}_4} = 25.0 \text{ g Na}_2\text{SO}_4 \times \frac{1 \text{ mol Na}_2\text{SO}_4}{142.0 \text{ g Na}_2\text{SO}_4}$$

Combining this equation with the first leads to

$$\text{amount Na}^+ = n_{\text{Na}^+} = 25.0 \text{ g Na}_2\text{SO}_4 \times \frac{1 \text{ mol Na}_2\text{SO}_4}{142.0 \text{ g Na}_2\text{SO}_4} \times \frac{2 \text{ mol Na}^+}{\text{mol Na}_2\text{SO}_4}$$

To obtain the mass of sodium in 25.0 g of Na_2SO_4 , multiply the number of moles of Na^+ by the molar mass of Na^+ , or 22.99 g. And so,

$$\text{mass Na}^+ = \frac{\text{mol Na}^+}{\text{mol Na}^+} \times \frac{22.99 \text{ g Na}^+}{\text{mol Na}^+}$$

Substituting the previous equation gives the mass in grams of Na^+ :

$$\begin{aligned} \text{mass Na}^+ &= 25.0 \text{ g Na}_2\text{SO}_4 \times \frac{1 \text{ mol Na}_2\text{SO}_4}{142.0 \text{ g Na}_2\text{SO}_4} \times \frac{2 \text{ mol Na}^+}{\text{mol Na}_2\text{SO}_4} \times \frac{22.99 \text{ g Na}^+}{\text{mol Na}^+} \\ &= 8.10 \text{ g Na}^+ \end{aligned}$$

FEATURE 2-2**The Factor-Label Approach to Example 2-2**

Some students and instructors find it easier to write out the solution to a problem so that units in the denominator of each succeeding term eliminate the units in the numerator of the preceding one until the units of the answer are obtained. This method has been referred to as the **factor-label method**, **dimensional analysis**, or the **picket fence method**. For instance, in Example 2-2, the units of the answer are g Na⁺, and the units given are g Na₂SO₄. Thus, we can write

$$25.0 \text{ g } \cancel{\text{Na}_2\text{SO}_4} \times \frac{\text{mol Na}_2\text{SO}_4}{142.0 \text{ g } \cancel{\text{Na}_2\text{SO}_4}}$$

First eliminate moles of Na₂SO₄

$$25.0 \text{ g } \cancel{\text{Na}_2\text{SO}_4} \times \frac{\text{mol } \cancel{\text{Na}_2\text{SO}_4}}{142.0 \text{ g } \cancel{\text{Na}_2\text{SO}_4}} \times \frac{2 \text{ mol Na}^+}{\text{mol } \cancel{\text{Na}_2\text{SO}_4}}$$

and then eliminate moles of Na⁺. The result is:

$$25.0 \text{ g } \cancel{\text{Na}_2\text{SO}_4} \times \frac{1 \text{ mol } \cancel{\text{Na}_2\text{SO}_4}}{142.0 \text{ g } \cancel{\text{Na}_2\text{SO}_4}} \times \frac{2 \text{ mol } \cancel{\text{Na}^+}}{\text{mol } \cancel{\text{Na}_2\text{SO}_4}} \times \frac{22.99 \text{ g Na}^+}{\text{mol } \cancel{\text{Na}^+}} = 8.10 \text{ g Na}^+$$

2B Solutions and Their Concentrations

Over the course of history, measurements and their corresponding units were invented at the local level. By necessity of primitive communication and local technology, standards were nearly nonexistent, and conversions among the many systems were difficult.¹ The result was many hundreds of distinct ways of expressing concentrations of solutions. Fortunately for us, the advent of rapid communications technology and the development of efficient travel have forced globalization of measurement science and, along with it, the definition of global measurement standards. No field has enjoyed more benefit in this regard than chemistry in general and analytical chemistry in particular. Even so, we use a number of methods for expressing concentration.

2B-1 Concentration of Solutions

There are four fundamental ways of expressing solution concentration: molar concentration, percent concentration, solution-diluent volume ratio, and p-functions.

Molar Concentration

The **molar concentration** c_x of a solution of a solute species X is the number of moles of that species that is contained in 1 L of the solution (*not 1 L of the solvent*).

In terms of the number of moles of solute, n , and the volume, V , of solution, write

$$c_x = \frac{n_x}{V} \quad (2-2)$$

$$\text{molar concentration} = \frac{\text{no. moles solute}}{\text{volume in liters}}$$

¹In a humorous (and perhaps geeky) parody of local proliferation of measurement units, Robinson Crusoe's friend Friday measured moles in units of chipmunks and volume in old goat bladders. See J. E. Bissey, *J. Chem. Educ.*, **1969**, *46* (8), 497, DOI: 10.1021/ed046p497.

The unit of molar concentration is **molar**, symbolized by **M**, which has the dimensions of mol/L, or mol L⁻¹. Molar concentration is also the number of millimoles of solute per milliliter of solution.

$$1 \text{ M} = 1 \text{ mol L}^{-1} = 1 \frac{\text{mol}}{\text{L}} = 1 \text{ mmol mL}^{-1} = 1 \frac{\text{mmol}}{\text{mL}}$$

EXAMPLE 2-3

Calculate the molar concentration of ethanol in an aqueous solution that contains 2.30 g of C₂H₅OH (46.07 g/mol) in 3.50 L of solution.

Solution

To calculate molar concentration, we must find both the amount of ethanol and the volume of the solution. The volume is given as 3.50 L, so all we need to do is to convert the mass of ethanol to the corresponding amount of ethanol in moles.

$$\begin{aligned} \text{amount C}_2\text{H}_5\text{OH} = n_{\text{C}_2\text{H}_5\text{OH}} &= 2.30 \text{ g C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g C}_2\text{H}_5\text{OH}} \\ &= 0.04992 \text{ mol C}_2\text{H}_5\text{OH} \end{aligned}$$

To obtain the molar concentration, $c_{\text{C}_2\text{H}_5\text{OH}}$, divide the amount by the volume. Thus,

$$\begin{aligned} c_{\text{C}_2\text{H}_5\text{OH}} &= \frac{2.30 \text{ g C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g C}_2\text{H}_5\text{OH}}}{3.50 \text{ L}} \\ &= 0.0143 \text{ mol C}_2\text{H}_5\text{OH/L} = 0.0143 \text{ M} \end{aligned}$$

There are two ways of expressing molar concentration: molar analytical concentration and molar equilibrium concentration. The distinction between these two expressions is in whether the solute undergoes chemical change in the solution process.

Molar Analytical Concentration

The **molar analytical concentration**, or for the sake of brevity, just **analytical concentration**, of a solution gives the *total* number of moles of a solute in 1 L of the solution (or the total number of millimoles in 1 mL). In other words, the molar analytical concentration specifies a recipe by which the solution can be prepared regardless of what might happen to the solute during the solution process. Note that in Example 2-3, the molar concentration that we calculated is also the molar analytical concentration $c_{\text{C}_2\text{H}_5\text{OH}} = 0.0143 \text{ M}$ because the solute ethanol molecules are unchanged following the solution process.

In another example, a sulfuric acid solution that has an analytical concentration of $c_{\text{H}_2\text{SO}_4} = 1.0 \text{ M}$ can be prepared by dissolving 1.0 mole, or 98 g, of H₂SO₄ in water and diluting the acid to exactly 1.0 L. There are important differences between the ethanol and sulfuric acid examples.

Molar analytical concentration is the total number of moles of a solute, regardless of its chemical state, in 1 L of solution. The molar analytical concentration describes how a solution of a given concentration can be prepared.

Molar equilibrium concentration is the molar concentration of a particular species in a solution.

In your study of chemistry, you will find that terminology constantly evolves as we refine our understanding of the processes that we study and endeavor to describe them more accurately. Molarity, which is a synonym for molar concentration, is an example of a term that is rapidly going out of fashion. Although you may find a few occurrences of molarity as a synonym for molar concentration in this textbook, we avoid it whenever possible.

The IUPAC recommends the general term *concentration* to express the composition of a solution with respect to its volume, with four subterms: amount concentration, mass concentration, volume concentration, and number concentration. Molar concentration, molar analytical concentration, and molar equilibrium concentration are all amount concentrations by this definition.

In this example, the *molar analytical concentration* of H_2SO_4 is given by

$$c_{\text{H}_2\text{SO}_4} = [\text{SO}_4^{2-}] + [\text{HSO}_4^-]$$

because SO_4^{2-} and HSO_4^- are the only two sulfate-containing species in the solution. The *molar equilibrium concentrations* of the ions are $[\text{SO}_4^{2-}]$ and $[\text{HSO}_4^-]$.

Molar Equilibrium Concentration

The **molar equilibrium concentration**, or just **equilibrium concentration**, refers to the molar concentration of a *particular species* in a solution at equilibrium. To specify the molar equilibrium concentration of a species, it is necessary to know how the solute behaves when it is dissolved in a solvent. For example, the molar equilibrium concentration of H_2SO_4 in a solution with a molar analytical concentration $c_{\text{H}_2\text{SO}_4} = 1.0 \text{ M}$ is actually 0.0 M because the sulfuric acid is completely dissociated into a mixture of H^+ , HSO_4^- , SO_4^{2-} ions. There are essentially no H_2SO_4 molecules in this solution. The equilibrium concentrations of the ions are 1.01 , 0.99 , and 0.01 M , respectively.

Equilibrium molar concentrations are usually symbolized by placing square brackets around the chemical formula for the species. So, for the solution of H_2SO_4 with an analytical concentration of $c_{\text{H}_2\text{SO}_4} = 1.0 \text{ M}$, write

$$\begin{aligned} [\text{H}_2\text{SO}_4] &= 0.00 \text{ M} & [\text{H}^+] &= 1.01 \text{ M} \\ [\text{HSO}_4^-] &= 0.99 \text{ M} & [\text{SO}_4^{2-}] &= 0.01 \text{ M} \end{aligned}$$

EXAMPLE 2-4

Calculate the analytical and equilibrium molar concentrations of the solute species in an aqueous solution that contains 285 mg of trichloroacetic acid, Cl_3CCOOH (163.4 g/mol), in 10.0 mL (the acid is 73% ionized in water).

Solution

As in Example 2-3, we calculate the number of moles of Cl_3CCOOH , which we designate as HA, and divide by the volume of the solution, 10.0 mL , or 0.0100 L . Therefore,

$$\begin{aligned} \text{amount HA} = n_{\text{HA}} &= 285 \text{ mg HA} \times \frac{1 \text{ g HA}}{1000 \text{ mg HA}} \times \frac{1 \text{ mol HA}}{163.4 \text{ g HA}} \\ &= 1.744 \times 10^{-3} \text{ mol HA} \end{aligned}$$

The molar analytical concentration, c_{HA} , is then

$$c_{\text{HA}} = \frac{1.744 \times 10^{-3} \text{ mol HA}}{10.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.174 \frac{\text{mol HA}}{\text{L}} = 0.174 \text{ M}$$

In this solution, 73% of the HA dissociates, giving H^+ and A^- :



The equilibrium concentration of HA is then 27% of c_{HA} . Thus,

$$\begin{aligned} [\text{HA}] &= c_{\text{HA}} \times (100 - 73)/100 = 0.174 \times 0.27 = 0.047 \text{ mol/L} \\ &= 0.047 \text{ M} \end{aligned}$$

The equilibrium concentration of A^- is equal to 73% of the analytical concentration of HA, that is,

$$[\text{A}^-] = \frac{73 \text{ mol A}^-}{100 \text{ mol HA}} \times 0.174 \frac{\text{mol HA}}{\text{L}} = 0.127 \text{ M}$$

(continued)

Because 1 mole of H^+ is formed for each mole of A^- , we can also write

$$[\text{H}^+] = [\text{A}^-] = 0.127 \text{ M}$$

and

$$c_{\text{HA}} = [\text{HA}] + [\text{A}^-] = 0.047 + 0.127 = 0.174 \text{ M}$$



Molecular model of trichloroacetic acid, Cl_3CCOOH . The rather strong acidity of trichloroacetic acid is usually ascribed to the inductive effect of the three chlorine atoms attached to the end of the molecule opposite the acidic proton. Electron density is withdrawn from the carboxylate group so that the trichloroacetate anion formed when the acid dissociates is stabilized. The acid is used in protein precipitation and in dermatological preparations for the removal of undesirable skin growths.

EXAMPLE 2-5

Describe the preparation of 2.00 L of 0.108 M BaCl_2 from $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (244.3 g/mol).

Solution

To determine the mass of solute to be dissolved and diluted to 2.00 L, note that 1 mole of the dihydrate yields 1 mole of BaCl_2 in solution. Therefore, to produce this solution, we need

$$2.00 \text{ L} \times \frac{0.108 \text{ mol BaCl}_2 \cdot 2\text{H}_2\text{O}}{\text{L}} = 0.216 \text{ mol BaCl}_2 \cdot 2\text{H}_2\text{O}$$

The mass of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ is then

$$0.216 \text{ mol BaCl}_2 \cdot 2\text{H}_2\text{O} \times \frac{244.3 \text{ g BaCl}_2 \cdot 2\text{H}_2\text{O}}{\text{mol BaCl}_2 \cdot 2\text{H}_2\text{O}} = 52.8 \text{ g BaCl}_2 \cdot 2\text{H}_2\text{O}$$

Dissolve 52.8 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in water and dilute to 2.00 L.

EXAMPLE 2-6

Describe the preparation of 500 mL of 0.0740 M Cl^- solution from solid $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (244.3 g/mol).

Solution

$$\begin{aligned} \text{mass BaCl}_2 \cdot 2\text{H}_2\text{O} &= \frac{0.0740 \text{ mol Cl}^-}{\text{L}} \times 0.500 \text{ L} \times \frac{1 \text{ mol BaCl}_2 \cdot 2\text{H}_2\text{O}}{2 \text{ mol Cl}^-} \\ &\times \frac{244.3 \text{ g BaCl}_2 \cdot 2\text{H}_2\text{O}}{\text{mol BaCl}_2 \cdot 2\text{H}_2\text{O}} = 4.52 \text{ g BaCl}_2 \cdot 2\text{H}_2\text{O} \end{aligned}$$

Dissolve 4.52 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in water and dilute to 0.500 L or 500 mL.

The number of moles of the species A in a solution of A is given by

$$\text{no. mol A} = n_A = c_A \times V_A$$

$$\text{mol}_A = \frac{\text{mol}_A}{\text{L}} \times \text{L}$$

where V_A is the volume of the solution in liters.

Percent Concentration

We sometimes express concentrations in terms of percent (parts per hundred). Unfortunately, this practice can be a source of ambiguity because percent composition of a solution can be expressed in several ways. Three common methods are

$$\text{weight percent (w/w)} = \frac{\text{weight solute}}{\text{weight solution}} \times 100\%$$

$$\text{volume percent (v/v)} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\%$$

$$\text{weight/volume percent (w/v)} = \frac{\text{weight solute, g}}{\text{volume solution, mL}} \times 100\%$$

Weight percent should more properly be called *mass percent* and abbreviated m/m. The term *weight percent* is so widely used in the chemical literature, however, that we will use it throughout this text. In IUPAC terminology, weight percent is mass concentration.

In IUPAC terminology, volume percent is volume concentration.

Always specify the type of percent when reporting concentrations in this way.

In IUPAC terminology, parts per billion, parts per million, and parts per thousand are mass concentrations.

A handy rule in calculating parts per million is to remember that for dilute aqueous solutions whose densities are approximately 1.00 g/mL, 1 ppm = 1.00 mg/L. That is,

$$c_{\text{ppm}} = \frac{\text{mass solute (g)}}{\text{mass solution (g)}} \times 10^6 \text{ ppm}$$

$$c_{\text{ppm}} = \frac{\text{mass solute (mg)}}{\text{volume solution (L)}} \text{ ppm} \quad (2-3)$$

Note that the denominator in each of these expressions is the mass or volume of *solution* rather than mass or volume of solvent. Note also that the first two expressions do not depend on the units used for weight (mass) or volume as long as the same units are used in the numerator and the denominator. In the third expression, units must be defined because the numerator and denominator have different units that do not cancel. Of the three expressions, only weight percent has the advantage of being temperature independent.

Weight percent is often used to express the concentration of commercial aqueous reagents. For example, nitric acid is sold as a 70% (w/w) solution, meaning that the reagent contains 70 g of HNO₃ per 100 g of solution (see Example 2-10).

Volume percent is commonly used to specify the concentration of a solution prepared by diluting a pure liquid compound with another liquid. For example, a 5% (v/v) aqueous solution of methanol *usually* describes a solution prepared by diluting 5.0 mL of pure methanol with enough water to give 100 mL.

Weight or volume percent is often used to indicate the composition of dilute aqueous solutions of solid reagents. For example, 5% (w/v) aqueous silver nitrate *often* refers to a solution prepared by dissolving 5 g of silver nitrate in sufficient water to give 100 mL of solution.

To avoid uncertainty, always specify explicitly the type of percent composition being discussed. If this information is missing, the investigator must decide intuitively which of the several types is to be used. The potential error resulting from a wrong choice is considerable. For example, commercial 50% (w/w) sodium hydroxide contains 763 g NaOH per liter, which corresponds to 76.3% (w/v) sodium hydroxide.

Parts per Million and Parts per Billion

For very dilute solutions, **parts per million** (ppm) is a convenient way to express concentration:

$$c_{\text{ppm}} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \text{ ppm}$$

where c_{ppm} is the concentration in parts per million. The units of mass in the numerator and denominator must agree so that they cancel. For even more dilute solutions, 10⁹ ppb rather than 10⁶ ppm is used in the previous equation to give the results in **parts per billion** (ppb). The term **parts per thousand** (ppt) is also used, especially in oceanography.

EXAMPLE 2-7

What is the molar concentration of K⁺ in a solution that contains 63.3 ppm of K₃Fe(CN)₆ (329.3 g/mol)?

(continued)

Solution

Because the solution is so dilute, it is reasonable to assume that its density is 1.00 g/mL. Therefore, according to Equation 2-2,

$$\begin{aligned}
 63.3 \text{ ppm K}_3\text{Fe(CN)}_6 &= 63.3 \text{ mg K}_3\text{Fe(CN)}_6/\text{L} \\
 \frac{\text{no. mol K}_3\text{Fe(CN)}_6}{\text{L}} &= \frac{63.3 \text{ mg K}_3\text{Fe(CN)}_6}{\text{L}} \times \frac{1 \text{ g K}_3\text{Fe(CN)}_6}{1000 \text{ mg K}_3\text{Fe(CN)}_6} \\
 &\quad \times \frac{1 \text{ mol K}_3\text{Fe(CN)}_6}{329.3 \text{ g K}_3\text{Fe(CN)}_6} = 1.922 \times 10^{-4} \frac{\text{mol}}{\text{L}} \\
 &= 1.922 \times 10^{-4} \text{ M} \\
 [\text{K}^+] &= \frac{1.922 \times 10^{-4} \text{ mol K}_3\text{Fe(CN)}_6}{\text{L}} \times \frac{3 \text{ mol K}^+}{1 \text{ mol K}_3\text{Fe(CN)}_6} \\
 &= 5.77 \times 10^{-4} \frac{\text{mol K}^+}{\text{L}} = 5.77 \times 10^{-4} \text{ M}
 \end{aligned}$$

Solution-Diluent Volume Ratios

The composition of a dilute solution is sometimes specified in terms of the volume of a more concentrated solution and the volume of solvent used in diluting it. The volume of the former is separated from that of the latter by a colon. Thus, a 1:4 HCl solution contains four volumes of water for each volume of concentrated hydrochloric acid. This method of notation is frequently ambiguous in that the concentration of the original solution is not always obvious. Moreover, under some circumstances 1:4 means dilute one volume with three volumes. Because of such uncertainties, you should avoid using solution-diluent ratios.

p-Functions

Scientists frequently express the concentration of a species in terms of its **p-function**, or **p-value**. The p-value is the negative logarithm (to the base 10) of the molar concentration of that species. Thus, for the species X,

$$\text{pX} = -\log [\text{X}]$$

As shown by the following examples, p-values offer the advantage of allowing concentrations that vary over 10 or more orders of magnitude to be expressed in terms of small positive numbers.

EXAMPLE 2-8

Calculate the p-value for each ion in a solution that is $2.00 \times 10^{-3} \text{ M}$ in NaCl and $5.4 \times 10^{-4} \text{ M}$ in HCl.

Solution

$$\text{pH} = -\log [\text{H}^+] = -\log (5.4 \times 10^{-4}) = 3.27$$

To obtain pNa, write

$$\text{pNa} = -\log [\text{Na}^+] = -\log (2.00 \times 10^{-3}) = -\log (2.00 \times 10^{-3}) = 2.699$$

(continued)

Analysis of the units shows that

$$\begin{aligned}
 \frac{\text{g}}{\text{g}} &= \frac{\text{g}}{\text{g}} \times \frac{\overbrace{\text{g}}^{\text{Density of solution}}}{\text{mL}} \times \frac{\overbrace{10^3 \text{ mg}}^{\text{Conversion Factor}}}{1 \text{ g}} \times \frac{\overbrace{10^3 \text{ mL}}^{\text{Conversion Factor}}}{1 \text{ L}} = \\
 &10^6 \frac{\text{mg}}{\text{L}}
 \end{aligned}$$

In other words, the mass concentration expressed in g/g is a factor of 10^6 larger than the mass concentration expressed in mg/L. Therefore, the mass concentration in ppm is equivalent to that in mg/L. If it is expressed in g/g, we must multiply the ratio by 10^6 ppm.

For parts per billion, ppb

$$\begin{aligned}
 c_{\text{ppb}} &= \frac{\text{mass solute (g)}}{\text{mass solution (g)}} \\
 &\quad \times 10^9 \text{ ppb}
 \end{aligned}$$

$$c_{\text{ppb}} = \frac{\text{mass solute } (\mu\text{g})}{\text{volume solution (g)}} \text{ ppb}$$

For mass concentration in ppb, convert the units to $\mu\text{g/L}$ and use ppb.

◀ The best-known p-function is pH, which is the negative logarithm of $[\text{H}^+]$. We discuss the nature of H^+ , its nature in aqueous solution, and the alternative representation H_3O^+ in Section 7A-2.



Molecular model of HCl. Hydrogen chloride is a gas consisting of heteronuclear diatomic molecules. The gas is extremely soluble in water; when a solution of the gas is prepared, only then do the molecules dissociate to form aqueous hydrochloric acid, which consists of H_3O^+ and Cl^- ions. See Figure 7-1 and the accompanying discussion of the nature of H_3O^+ .

Density expresses the mass of a substance per unit volume. In SI units, density is expressed in units of kg/L or alternatively g/mL.

Specific gravity is the ratio of the mass of a substance to the mass of an equal volume of water.

The total Cl^- concentration is given by the sum of the concentrations of the two solutes:

$$\begin{aligned}[\text{Cl}^-] &= 2.00 \times 10^{-3} \text{ M} + 5.4 \times 10^{-4} \text{ M} \\ &= 2.00 \times 10^{-3} \text{ M} + 0.54 \times 10^{-3} \text{ M} = 2.54 \times 10^{-3} \text{ M} \\ \text{pCl} &= -\log[\text{Cl}^-] = -\log 2.54 \times 10^{-3} = 2.595\end{aligned}$$

Note that in Example 2-8, and in the one that follows, the results are rounded according to the rules listed on page 73, Section 4D-3.

EXAMPLE 2-9

Calculate the molar concentration of Ag^+ in a solution that has a pAg of 6.372.

Solution

$$\begin{aligned}\text{pAg} &= -\log[\text{Ag}^+] = 6.372 \\ \log[\text{Ag}^+] &= -6.372 \\ [\text{Ag}^+] &= 4.246 \times 10^{-7} \approx 4.25 \times 10^{-7} \text{ M}\end{aligned}$$

2B-2 Density and Specific Gravity of Solutions

Density and *specific gravity* are related terms often found in the analytical literature. The **density** of a substance is its mass per unit volume, and its **specific gravity** is the ratio of its mass to the mass of an equal volume of water at 4°C . Density has units of kilograms per liter or grams per milliliter in the metric system. Specific gravity is dimensionless and so is not tied to any particular system of units. For this reason, specific gravity is widely used in describing items of commerce (see **Figure 2-1**). Since the density of water is approximately 1.00 g/mL and since we use the metric system throughout this text, we use density and specific gravity interchangeably. The specific gravities of some concentrated acids and bases are given in **Table 2-3**.

EXAMPLE 2-10

Calculate the molar concentration of HNO_3 (63.0 g/mol) in a solution that has a specific gravity of 1.42 and is 70.5% HNO_3 (w/w).

Solution

First, calculate the mass of acid per liter of concentrated solution

$$\frac{\text{g HNO}_3}{\text{L reagent}} = \frac{1.42 \text{ kg reagent}}{\text{L reagent}} \times \frac{10^3 \text{ g reagent}}{\text{kg reagent}} \times \frac{70.5 \text{ g HNO}_3}{100 \text{ g reagent}} = \frac{1001 \text{ g HNO}_3}{\text{L reagent}}$$

Then,

$$c_{\text{HNO}_3} = \frac{1001 \text{ g HNO}_3}{\text{L reagent}} \times \frac{1 \text{ mol HNO}_3}{63.0 \text{ g HNO}_3} = \frac{15.9 \text{ mol HNO}_3}{\text{L reagent}} \approx 16 \text{ M}$$



Source: Courtesy of Avantor, Radnor, PA.

FIGURE 2-1 Label from a bottle of reagent-grade hydrochloric acid. Note that the specific gravity of the acid over the temperature range of 60° to 80°F is specified on the label. (Courtesy of Avantor Performance Materials, Radnor, PA.)

TABLE 2-3

Specific Gravities of Commercial Concentrated Acids and Bases

Reagent	Concentration, % (w/w)	Specific Gravity
Acetic acid	99.7	1.05
Ammonia	29.0	0.90
Hydrochloric acid	37.2	1.19
Hydrofluoric acid	49.5	1.15
Nitric acid	70.5	1.42
Perchloric acid	71.0	1.67
Phosphoric acid	86.0	1.71
Sulfuric acid	96.5	1.84

EXAMPLE 2-11

Describe the preparation of 100 mL of 6.0 M HCl from a concentrated solution that has a specific gravity of 1.18 and is 37% (w/w) HCl (36.5 g/mol).

Solution

Proceeding as in Example 2-10, first calculate the molar concentration of the concentrated reagent. Then calculate the number of moles of acid needed for the

(continued)

diluted solution. Finally, divide the second figure by the first to obtain the volume of concentrated acid required. Thus, to obtain the concentration of the reagent, write

$$c_{\text{HCl}} = \frac{1.18 \times 10^3 \text{ g reagent}}{\text{L reagent}} \times \frac{37 \text{ g HCl}}{100 \text{ g reagent}} \times \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} = 12.0 \text{ M}$$

The number of moles HCl required is given by

$$\text{no. mol HCl} = 100 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{6.0 \text{ mol HCl}}{\text{L}} = 0.600 \text{ mol HCl}$$

Finally, to obtain the volume of concentrated reagent, write

$$\text{vol concd reagent} = 0.600 \text{ mol HCl} \times \frac{1 \text{ L reagent}}{12.0 \text{ mol HCl}} = 0.0500 \text{ L or } 50.0 \text{ mL}$$

Therefore, dilute 50 mL of the concentrated reagent to 600 mL.

The solution to Example 2-11 is based on the following useful relationship, which we use often:

$$V_{\text{concd}} \times c_{\text{concd}} = V_{\text{dil}} \times c_{\text{dil}} \quad (2-4)$$

where the two terms on the left are the volume and molar concentration of a concentrated solution that is being used to prepare a diluted solution having the volume and concentration given by the corresponding terms on the right. This equation is based on the fact that the number of moles of solute in the diluted solution must equal the number of moles in the concentrated reagent. Note that the volumes can be in milliliters or liters as long as the same units are used for both solutions.

Equation 2-4 can be used with L and mol/L or mL and mmol/mL. >

Thus,

$$L_{\text{concd}} \times \frac{\text{mol}_{\text{concd}}}{L_{\text{concd}}} = L_{\text{dil}} \times \frac{\text{mol}_{\text{dil}}}{L_{\text{dil}}}$$

$$\text{mL}_{\text{concd}} \times \frac{\text{mmol}_{\text{concd}}}{\text{mL}_{\text{concd}}} = \text{mL}_{\text{dil}}$$

$$\times \frac{\text{mmol}_{\text{dil}}}{\text{mL}_{\text{dil}}}$$

The **stoichiometry** of a reaction is the relationship among the number of moles of reactants and products as represented by a balanced chemical equation.

2C Chemical Stoichiometry

Stoichiometry is the quantitative relationship among the amounts of reacting chemical species. This section provides a brief review of stoichiometry and its applications to chemical calculations.

2C-1 Empirical Formulas and Molecular Formulas

An **empirical formula** gives the simplest whole number ratio of atoms in a chemical compound. In contrast, a **molecular formula** specifies the number of atoms in a molecule. Two or more substances may have the same empirical formula but different molecular formulas. For example, CH_2O is both the empirical and the molecular formula for formaldehyde; it is also the empirical formula for such diverse substances as acetic acid, $\text{C}_2\text{H}_4\text{O}_2$; glyceraldehyde, $\text{C}_3\text{H}_6\text{O}_3$; and glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, as well as more than 50 other substances containing 6 or fewer carbon atoms. We may calculate the empirical formula of a compound from its percent composition. To determine the molecular formula, we must know the molar mass of the compound.