Chapter 2

Basic Tools of Analytical Chemistry

Chapter Overview

In the chapters that follow we will explore many aspects of analytical chemistry. In the process we will consider important questions, such as "How do we extract useful results from experimental data?", "How do we ensure our results are accurate?", "How do we obtain a representative sample?", and "How do we select an appropriate analytical technique?" Before we consider these and other questions, we first must review some basic tools of importance to analytical chemists.

It is important for scientists to agree upon a common set of units. In 1999, for example, NASA lost a Mar's Orbiter spacecraft because one engineering team used English units in their calculations and another engineering team used metric units. As a result, the spacecraft came too close to the planet's surface, causing its propulsion system to overheat and fail.

Some measurements, such as absorbance, do not have units. Because the meaning of a unitless number often is unclear, some authors include an artificial unit. It is not unusual to see the abbreviation AU—short for absorbance unit—following an absorbance value, which helps clarify that the measurement is an absorbance value.

There is some disagreement on the use of "amount of substance" to describe the measurement for which the mole is the base SI unit; see "What's in a Name? Amount of Substance, Chemical Amount, and Stoichiometric Amount," the full reference for which is Giunta, C. J. *J. Chem. Educ.* **2016**, *93*, 583–586.

2A   Measurements in Analytical Chemistry

Analytical chemistry is a quantitative science. Whether determining the concentration of a species, evaluating an equilibrium constant, measuring a reaction rate, or drawing a correlation between a compound's structure and its reactivity, analytical chemists engage in "measuring important chemical things."[1] In this section we review briefly the basic units of measurement and the proper use of significant figures.

2A.1   Units of Measurement

A measurement usually consists of a unit and a number that expresses the quantity of that unit. We can express the same physical measurement with different units, which creates confusion if we are not careful to specify the unit. For example, the mass of a sample that weighs 1.5 g is equivalent to 0.0033 lb or to 0.053 oz. To ensure consistency, and to avoid problems, scientists use the common set of fundamental base units listed in Table 2.1. These units are called SI UNITS after the Système International d'Unités.

We define other measurements using these fundamental SI units. For example, we measure the quantity of heat produced during a chemical reaction in joules, (J), where 1 J is equivalent to 1 m^2kg/s^2. Table 2.2 provides

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1   Murray, R. W. *Anal. Chem.* **2007**, *79*, 1765.

Table 2.1 Fundamental Base SI Units			
Measurement	Unit	Symbol	Definition (1 unit is...)
mass	kilogram	kg	...the mass of the international prototype, a Pt-Ir object housed at the Bureau International de Poids and Measures at Sèvres, France.[†]
distance	meter	m	...the distance light travels in $(299\ 792\ 458)^{-1}$ seconds.
temperature	Kelvin	K	...equal to $(273.16)^{-1}$, where 273.16 K is the triple point of water (where its solid, liquid, and gaseous forms are in equilibrium).
time	second	s	...the time it takes for 9 192 631 770 periods of radiation corresponding to a specific transition of the ^{133}Cs atom.
current	ampere	A	...the current producing a force of 2×10^{-7} N/m between two straight parallel conductors of infinite length separated by one meter (in a vacuum).
amount of substance	mole	mol	...the amount of a substance containing as many particles as there are atoms in exactly 0.012 kilogram of ^{12}C.
light	candela	cd	...the luminous intensity of a source with a monochromatic frequency of 540×10^{12} hertz and a radiant power of $(683)^{-1}$ watts per steradian.

[†]   The mass of the international prototype changes at a rate of approximately 1 μg per year due to reversible surface contamination. The reference mass, therefore, is determined immediately after its cleaning using a specified procedure. Current plans call for retiring the international prototype and defining the kilogram in terms of Planck's constant; see http://www.nist.gov/pml/si-redef/kg_future.cfm for more details.

Table 2.2 Derived SI Units and Non-SI Units of Importance to Analytical Chemistry

Measurement	Unit	Symbol	Equivalent SI Units
length	angstrom (non-SI)	Å	$1\text{ Å} = 1 \times 10^{-10}\text{ m}$
volume	liter (non-SI)	L	$1\text{ L} = 10^{-3}\text{ m}^3$
force	newton (SI)	N	$1\text{ N} = 1\text{ m·kg/s}^2$
pressure	pascal (SI) atmosphere (non-SI)	Pa atm	$1\text{ Pa} = 1\text{ N/m}^2 = 1\text{ kg/(m·s}^2)$ $1\text{ atm} = 101\ 325\text{ Pa}$
energy, work, heat	joule (SI) calorie (non-SI) electron volt (non-SI)	J cal eV	$1\text{ J} = \text{N·m} = 1\text{ m}^2\text{·kg/s}^2$ $1\text{ cal} = 4.184\text{ J}$ $1\text{ eV} = 1.602\ 177\ 33 \times 10^{-19}\text{ J}$
power	watt (SI)	W	$1\text{ W} = 1\text{ J/s} = 1\text{ m}^2\text{·kg/s}^3$
charge	coulomb (SI)	C	$1\text{ C} = 1\text{ A·s}$
potential	volt (SI)	V	$1\text{ V} = 1\text{ W/A} = 1\text{ m}^2\text{·kg/(s}^3\text{·A)}$
frequency	hertz (SI)	Hz	$1\text{ Hz} = \text{s}^{-1}$
temperature	Celsius (non-SI)	°C	$°C = K - 273.15$

a list of some important derived SI units, as well as a few common non-SI units.

Chemists frequently work with measurements that are very large or very small. A mole contains 602 213 670 000 000 000 000 000 particles and some analytical techniques can detect as little as 0.000 000 000 000 001 g of a compound. For simplicity, we express these measurements using SCIENTIFIC NOTATION; thus, a mole contains $6.022\ 136\ 7 \times 10^{23}$ particles, and the detected mass is 1×10^{-15} g. Sometimes we wish to express a measurement without the exponential term, replacing it with a prefix (Table 2.3). A mass of 1×10^{-15} g, for example, is the same as 1 fg, or femtogram.

Writing a lengthy number with spaces instead of commas may strike you as unusual. For a number with more than four digits on either side of the decimal point, however, the recommendation from the International Union of Pure and Applied Chemistry is to use a thin space instead of a comma.

Table 2.3 Common Prefixes for Exponential Notation

Prefix	Symbol	Factor	Prefix	Symbol	Factor	Prefix	Symbol	Factor
yotta	Y	10^{24}	kilo	k	10^{3}	micro	μ	10^{-6}
zetta	Z	10^{21}	hecto	h	10^{2}	nano	n	10^{-9}
eta	E	10^{18}	deka	da	10^{1}	pico	p	10^{-12}
peta	P	10^{15}	-	-	10^{0}	femto	f	10^{-15}
tera	T	10^{12}	deci	d	10^{-1}	atto	a	10^{-18}
giga	G	10^{9}	centi	c	10^{-2}	zepto	z	10^{-21}
mega	M	10^{6}	milli	m	10^{-3}	yocto	y	10^{-24}

Figure 2.1 When weighing an sample on a balance, the measurement fluctuates in the final decimal place. We record this sample's mass as 0.5730 g ± 0.0001 g.

In the measurement **0.0**99**0** g, the zero in **green** is a significant digit and the zeros in **red** are not significant digits.

2A.2   Uncertainty in Measurements

A measurement provides information about both its magnitude and its uncertainty. Consider, for example, the three photos in Figure 2.1, taken at intervals of approximately 1 sec after placing a sample on the balance. Assuming the balance is properly calibrated, we are certain that the sample's mass is more than 0.5729 g and less than 0.5731 g. We are uncertain, however, about the sample's mass in the last decimal place since the final two decimal places fluctuate between 29, 30, and 31. The best we can do is to report the sample's mass as 0.5730 g ± 0.0001 g, indicating both its magnitude and its absolute uncertainty.

SIGNIFICANT FIGURES

A measurement's SIGNIFICANT FIGURES convey information about a measurement's magnitude and uncertainty. The number of significant figures in a measurement is the number of digits known exactly plus one digit whose value is uncertain. The mass shown in Figure 2.1, for example, has four significant figures, three which we know exactly and one, the last, which is uncertain.

Suppose we weigh a second sample, using the same balance, and obtain a mass of 0.0990 g. Does this measurement have 3, 4, or 5 significant figures? The zero in the last decimal place is the one uncertain digit and is significant. The other two zero, however, simply indicate the decimal point's location. Writing the measurement in scientific notation (9.90×10^{-2}) clarifies that there are three significant figures in 0.0990.

Example 2.1

How many significant figures are in each of the following measurements? Convert each measurement to its equivalent scientific notation or decimal form.

(a) 0.0120 mol HCl
(b) 605.3 mg $CaCO_3$
(c) 1.043×10^{-4} mol Ag^+
(d) 9.3×10^4 mg NaOH

SOLUTION

(a) Three significant figures; 1.20×10^{-2} mol HCl.
(b) Four significant figures; 6.053×10^2 mg $CaCO_3$.
(c) Four significant figures; 0.000 104 3 mol Ag^+.
(d) Two significant figures; 93 000 mg NaOH.

There are two special cases when determining the number of significant figures in a measurement. For a measurement given as a logarithm, such as pH, the number of significant figures is equal to the number of digits to the right of the decimal point. Digits to the left of the decimal point are not

significant figures since they indicate only the power of 10. A pH of 2.45, therefore, contains two significant figures.

An exact number, such as a stoichiometric coefficient, has an infinite number of significant figures. A mole of $CaCl_2$, for example, contains exactly two moles of chloride ions and one mole of calcium ions. Another example of an exact number is the relationship between some units. There are, for example, exactly 1000 mL in 1 L. Both the 1 and the 1000 have an infinite number of significant figures.

Using the correct number of significant figures is important because it tells other scientists about the uncertainty of your measurements. Suppose you weigh a sample on a balance that measures mass to the nearest ± 0.1 mg. Reporting the sample's mass as 1.762 g instead of 1.7623 g is incorrect because it does not convey properly the measurement's uncertainty. Reporting the sample's mass as 1.76231 g also is incorrect because it falsely suggests an uncertainty of ± 0.01 mg.

SIGNIFICANT FIGURES IN CALCULATIONS

Significant figures are also important because they guide us when reporting the result of an analysis. When we calculate a result, the answer cannot be more certain than the least certain measurement in the analysis. Rounding an answer to the correct number of significant figures is important.

For addition and subtraction, we round the answer to the last decimal place in common for each measurement in the calculation. The exact sum of 135.621, 97.33, and 21.2163 is 254.1673. Since the last decimal place common to all three numbers is the hundredth's place

$$135.6\mathbf{2}1$$
$$97.3\mathbf{3}$$
$$21.2\mathbf{1}63$$
$$254.1\mathbf{6}73$$

we round the result to 254.17. When working with scientific notation, first convert each measurement to a common exponent before determining the number of significant figures. For example, the sum of 6.17×10^7, 4.3×10^5, and 3.23×10^4 is 6.22×10^7.

$$6.1\mathbf{7} \quad\ \times 10^7$$
$$0.0\mathbf{4}3 \quad \times 10^7$$
$$0.0\mathbf{0}323 \times 10^7$$
$$6.2\mathbf{1}623 \times 10^7$$

For multiplication and division, we round the answer to the same number of significant figures as the measurement with the fewest number of significant figures. For example, when we divide the product of 22.91 and 0.152 by 16.302, we report the answer as 0.214 (three significant figures) because 0.152 has the fewest number of significant figures.

The log of 2.8×10^2 is 2.45. The log of 2.8 is 0.45 and the log of 10^2 is 2. The 2 in 2.45, therefore, only indicates the power of 10 and is not a significant digit.

The last common decimal place shared by 135.621, 97.33, and 21.2163 is shown in **red**.

The last common decimal place shared by 4.3×10^5, 6.17×10^7, and 3.23×10^4 is shown in **red**.

$$\frac{22.91 \times 0.152}{16.302} = 0.2136 = 0.214$$

There is no need to convert measurements in scientific notation to a common exponent when multiplying or dividing.

Finally, to avoid "round-off" errors, it is a good idea to retain at least one extra significant figure throughout any calculation. Better yet, invest in a good scientific calculator that allows you to perform lengthy calculations without the need to record intermediate values. When your calculation is complete, round the answer to the correct number of significant figures using the following simple rules.

It is important to recognize that the rules presented here for working with significant figures are generalizations. What actually is conserved is uncertainty, not the number of significant figures. For example, the following calculation

101/99 = 1.02

is correct even though it violates the general rules outlined earlier. Since the relative uncertainty in each measurement is approximately 1% (101 ± 1 and 99 ± 1), the relative uncertainty in the final answer also is approximately 1%. Reporting the answer as 1.0 (two significant figures), as required by the general rules, implies a relative uncertainty of 10%, which is too large. The correct answer, with three significant figures, yields the expected relative uncertainty. Chapter 4 presents a more thorough treatment of uncertainty and its importance in reporting the result of an analysis.

1. Retain the least significant figure if it and the digits that follow are less than half way to the next higher digit. For example, rounding 12.442 to the nearest tenth gives 12.4 since 0.442 is less than half way between 0.400 and 0.500.

2. Increase the least significant figure by 1 if it and the digits that follow are more than half way to the next higher digit. For example, rounding 12.476 to the nearest tenth gives 12.5 since 0.476 is more than half way between 0.400 and 0.500.

3. If the least significant figure and the digits that follow are exactly half-way to the next higher digit, then round the least significant figure to the nearest even number. For example, rounding 12.450 to the nearest tenth gives 12.4, while rounding 12.550 to the nearest tenth gives 12.6. Rounding in this manner ensures that we round up as often as we round down.

Practice Exercise 2.1

For a problem that involves both addition and/or subtraction, and multiplication and/or division, be sure to account for significant figures at each step of the calculation. With this in mind, report the result of this calculation to the correct number of significant figures.

$$\frac{0.250 \times (9.93 \times 10^{-3}) - 0.100 \times (1.927 \times 10^{-2})}{9.93 \times 10^{-3} + 1.927 \times 10^{-2}} =$$

Click here to review your answer to this exercise.

2B   Concentration

CONCENTRATION is a general measurement unit that reports the amount of solute present in a known amount of solution

$$\text{concentration} = \frac{\text{amount of solute}}{\text{amount of solution}} \qquad 2.1$$

Although we associate the terms "solute" and "solution" with liquid samples, we can extend their use to gas-phase and solid-phase samples as well. Table 2.4 lists the most common units of concentration.

2B.1   Molarity and Formality

Both molarity and formality express concentration as moles of solute per liter of solution; however, there is a subtle difference between them. Molarity is the concentration of a particular chemical species. Formality, on the other hand, is a substance's total concentration without regard to its specific chemical form. There is no difference between a compound's molarity and formality if it dissolves without dissociating into ions. The formal concentration of a solution of glucose, for example, is the same as its molarity.

For a compound that ionizes in solution, such as $CaCl_2$, molarity and formality are different. When we dissolve 0.1 moles of $CaCl_2$ in 1 L of water, the solution contains 0.1 moles of Ca^{2+} and 0.2 moles of Cl^-. The molarity of $CaCl_2$, therefore, is zero since there is no undissociated $CaCl_2$ in solution; instead, the solution is 0.1 M in Ca^{2+} and 0.2 M in Cl^-. The formality of $CaCl_2$, however, is 0.1 F since it represents the total amount of $CaCl_2$ in solution. This more rigorous definition of molarity, for better or worse, largely is ignored in the current literature, as it is in this textbook. When we state that a solution is 0.1 M $CaCl_2$ we understand it to consist of Ca^{2+} and Cl^- ions. We will reserve the unit of formality to situations where it provides a clearer description of solution chemistry.

A solution that is 0.0259 M in glucose is 0.0259 F in glucose as well.

Table 2.4 Common Units for Reporting Concentration

Name	Units	Symbol
molarity	$\dfrac{\text{moles solute}}{\text{liters solution}}$	M
formality	$\dfrac{\text{moles solute}}{\text{liters solution}}$	F
normality	$\dfrac{\text{equivalents solute}}{\text{liters solution}}$	N
molality	$\dfrac{\text{moles solute}}{\text{kilograms solvent}}$	m
weight percent	$\dfrac{\text{grams solute}}{100 \text{ grams solution}}$	% w/w
volume percent	$\dfrac{\text{mL solute}}{100 \text{ mL solution}}$	% v/v
weight-to-volume percent	$\dfrac{\text{grams solute}}{100 \text{ mL solution}}$	% w/v
parts per million	$\dfrac{\text{grams solute}}{10^6 \text{ grams solution}}$	ppm
parts per billion	$\dfrac{\text{grams solute}}{10^9 \text{ grams solution}}$	ppb

An alternative expression for weight percent is

$$\frac{\text{grams solute}}{\text{grams solution}} \times 100$$

You can use similar alternative expressions for volume percent and for weight-to-volume percent.

Molarity is used so frequently that we use a symbolic notation to simplify its expression in equations and in writing. Square brackets around a species indicate that we are referring to that species' molarity. Thus, $[Ca^{2+}]$ is read as "the molarity of calcium ions."

2B.2 Normality

One handbook that still uses normality is *Standard Methods for the Examination of Water and Wastewater*, a joint publication of the American Public Health Association, the American Water Works Association, and the Water Environment Federation. This handbook is one of the primary resources for the environmental analysis of water and wastewater.

Normality is a concentration unit no longer in common use; however, because you may encounter normality in older handbooks of analytical methods, it is helpful to understand its meaning. Normality defines concentration in terms of an equivalent, which is the amount of one chemical species that reacts stoichiometrically with another chemical species. Note that this definition makes an equivalent, and thus normality, a function of the chemical reaction in which the species participates. Although a solution of H_2SO_4 has a fixed molarity, its normality depends on how it reacts. You will find a more detailed treatment of normality in Appendix 1.

2B.3 Molality

Molality is used in thermodynamic calculations where a temperature-independent unit of concentration is needed. Molarity is based on the volume of solution that contains the solute. Since density is a temperature dependent property, a solution's volume, and thus its molar concentration, changes with temperature. By using the solvent's mass in place of the solution's volume, the resulting concentration becomes independent of temperature.

2B.4 Weight, Volume, and Weight-to-Volume Percents

Weight percent (% w/w), volume percent (% v/v) and weight-to-volume percent (% w/v) express concentration as the units of solute present in 100 units of solution. A solution that is 1.5% w/v NH_4NO_3, for example, contains 1.5 gram of NH_4NO_3 in 100 mL of solution.

2B.5 Parts Per Million and Parts Per Billion

Parts per million (ppm) and parts per billion (ppb) are ratios that give the grams of solute in, respectively, one million or one billion grams of sample. For example, a sample of steel that is 450 ppm in Mn contains 450 μg of Mn for every gram of steel. If we approximate the density of an aqueous solution as 1.00 g/mL, then we can express solution concentrations in ppm or ppb using the following relationships.

$$\text{ppm} = \frac{\mu g}{g} = \frac{mg}{L} = \frac{\mu g}{mL} \qquad \text{ppb} = \frac{ng}{g} = \frac{\mu g}{L} = \frac{ng}{mL}$$

For gases a part per million usually is expressed as a volume ratio; for example, a helium concentration of 6.3 ppm means that one liter of air contains 6.3 μL of He.

2B.6   Converting Between Concentration Units

The most common ways to express concentration in analytical chemistry are molarity, weight percent, volume percent, weight-to-volume percent, parts per million and parts per billion. The general definition of concentration in equation 2.1 makes it is easy to convert between concentration units.

Example 2.2

A concentrated solution of ammonia is 28.0% w/w NH_3 and has a density of 0.899 g/mL. What is the molar concentration of NH_3 in this solution?

SOLUTION

$$\frac{28.0 \text{ g NH}_3}{100 \text{ g soln}} \times \frac{0.899 \text{ g soln}}{\text{mL soln}} \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \times \frac{1000 \text{ mL}}{\text{L}} = 14.8 \text{ M}$$

Example 2.3

The maximum permissible concentration of chloride ion in a municipal drinking water supply is 2.50×10^2 ppm Cl^-. When the supply of water exceeds this limit it often has a distinctive salty taste. What is the equivalent molar concentration of Cl^-?

SOLUTION

$$\frac{2.50 \times 10^2 \text{ mg Cl}^-}{\text{L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol Cl}^-}{35.453 \text{ g Cl}^-} = 7.05 \times 10^{-3} \text{ M}$$

Practice Exercise 2.2

Which solution—0.50 M NaCl or 0.25 M $SrCl_2$—has the larger concentration when expressed in μg/mL?

Click here to review your answer to this exercise.

2B.7   p-Functions

Sometimes it is inconvenient to use the concentration units in Table 2.4. For example, during a chemical reaction a species' concentration may change by many orders of magnitude. If we want to display the reaction's progress graphically we might wish to plot the reactant's concentration as a function of the volume of a reagent added to the reaction. Such is the case in Figure 2.2 for the titration of HCl with NaOH. The y-axis on the left-side of the figure displays the $[H^+]$ as a function of the volume of NaOH. The initial $[H^+]$ is 0.10 M and its concentration after adding 80 mL of NaOH is 4.3×10^{-13} M. We easily can follow the change in $[H^+]$ for the first 14

Acid–base titrations, as well as several other types of titrations, are covered in Chapter 9.

Figure 2.2 Two curves showing the progress of a titration of 50.0 mL of 0.10 M HCl with 0.10 M NaOH. The [H⁺] is shown on the left *y*-axis and the pH on the right *y*-axis.
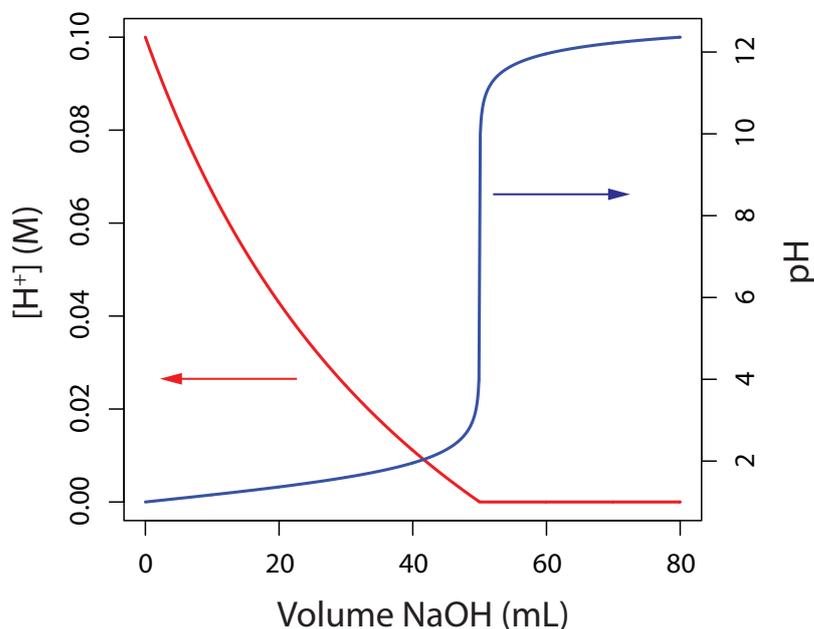
additions of NaOH; however, for the remaining additions of NaOH the change in $[H^+]$ is too small to see.

When working with concentrations that span many orders of magnitude, it often is more convenient to express concentration using a p-function. The p-function of X is written as pX and is defined as

$$pX = -\log(X)$$

The pH of a solution that is 0.10 M H⁺, for example, is

$$pH = -\log[H^+] = -\log(0.10) = 1.00$$

and the pH of 4.3×10^{-13} M H⁺ is

$$pH = -\log[H^+] = -\log(4.3 \times 10^{-13}) = 12.37$$

Figure 2.2 shows that plotting pH as a function of the volume of NaOH provides more useful information about how the concentration of H⁺ changes during the titration.

A more appropriate equation for pH is

$$pH = -\log(a_{H^+})$$

where a_{H^+} is the activity of the hydrogen ion. See Chapter 6I for more details. For now the approximate equation

$$pH = -\log[H^+]$$

is sufficient.

Example 2.4

What is pNa for a solution of 1.76×10^{-3} M Na_3PO_4?

SOLUTION

Since each mole of Na_3PO_4 contains three moles of Na⁺, the concentration of Na⁺ is

$$[Na^+] = (1.76 \times 10^{-3} \text{ M}) \times \frac{3 \text{ mol Na}^+}{\text{mol Na}_3PO_4} = 5.28 \times 10^{-3} \text{ M}$$

and pNa is

$$pNa = -\log[Na^+] = -\log(5.28 \times 10^{-3}) = 2.277$$

Example 2.5

What is the $[H^+]$ in a solution that has a pH of 5.16?

SOLUTION

The concentration of H^+ is

$$pH = -\log[H^+] = 5.16$$
$$\log[H^+] = -5.16$$
$$[H^+] = 10^{-5.16} = 6.9 \times 10^{-6} \text{ M}$$

If $\log(X) = a$, then $X = 10^a$.

Practice Exercise 2.3

What are the values for pNa and pSO_4 if we dissolve 1.5 g Na_2SO_4 in a total solution volume of 500.0 mL?

Click here to review your answer to this exercise.

2C   Stoichiometric Calculations

A balanced reaction, which defines the stoichiometric relationship between the moles of reactants and the moles of products, provides the basis for many analytical calculations. Consider, for example, an analysis for oxalic acid, $H_2C_2O_4$, in which Fe^{3+} oxidizes oxalic acid to CO_2

$$2Fe^{3+}(aq) + H_2C_2O_4(aq) + 2H_2O(l) \rightarrow$$
$$2Fe^{2+}(aq) + 2CO_2(g) + 2H_3O^+(aq)$$
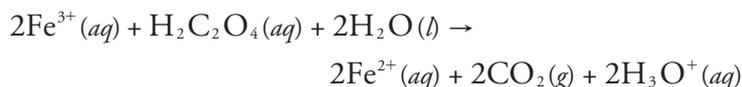
The balanced reaction shows us that one mole of oxalic acid reacts with two moles of Fe^{3+}. As shown in the following example, we can use this balanced reaction to determine the amount of $H_2C_2O_4$ in a sample of rhubarb if we know the moles of Fe^{3+} needed to react completely with oxalic acid.
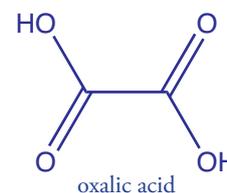
oxalic acid

Example 2.6

The amount of oxalic acid in a sample of rhubarb was determined by reacting with Fe^{3+}. After extracting a 10.62 g of rhubarb with a solvent, oxidation of the oxalic acid required 36.44 mL of 0.0130 M Fe^{3+}. What is the weight percent of oxalic acid in the sample of rhubarb?

SOLUTION

We begin by calculating the moles of Fe^{3+} used in the reaction

$$\frac{0.0130 \text{ mol Fe}^{3+}}{L} \times 0.03644 \text{ L} = 4.737 \times 10^{-4} \text{ mol Fe}^{3+}$$

Oxalic acid, in sufficient amounts, is toxic. At lower physiological concentrations it leads to the formation of kidney stones. The leaves of the rhubarb plant contain relatively high concentrations of oxalic acid. The stalk, which many individuals enjoy eating, contains much smaller concentrations of oxalic acid.

The moles of oxalic acid reacting with the Fe^{3+}, therefore, is

$$4.73\mathbf{7} \times 10^{-4}\, mol\, Fe^{3+} \times \frac{1\, mol\, H_2C_2O_4}{2\, mol\, Fe^{3+}} = 2.36\mathbf{8} \times 10^{-4}\, mol\, H_2C_2O_4$$

Converting the moles of oxalic acid to grams of oxalic acid

$$2.36\mathbf{8} \times 10^{-4}\, mol\, H_2C_2O_4 \times \frac{90.03\, g\, H_2C_2O_4}{mol\, H_2C_2O_4} =$$
$$2.13\mathbf{2} \times 10^{-2}\, g\, H_2C_2O_4$$

and calculating the weight percent gives the concentration of oxalic acid in the sample of rhubarb as

$$\frac{2.13\mathbf{2} \times 10^{-2}\, g\, H_2C_2O_4}{10.62\, g\, rhubarb} \times 100 = 0.201\%\, w/w\, H_2C_2O_4$$

Practice Exercise 2.4

You can dissolve a precipitate of AgBr by reacting it with $Na_2S_2O_3$, as shown here.

$$AgBr\,(s) + 2Na_2S_2O_3\,(aq) \rightarrow Ag\,(S_2O_3)_2{}^{3-}\,(aq) + Br^-\,(aq) + 4Na^+\,(aq)$$

How many mL of 0.0138 M $Na_2S_2O_3$ do you need to dissolve 0.250 g of AgBr?

Click here to review your answer to this question.

The analyte in Example 2.6, oxalic acid, is in a chemically useful form because there is a reagent, Fe^{3+}, that reacts with it quantitatively. In many analytical methods, we first must convert the analyte into a more accessible form before we can complete the analysis. For example, one method for the quantitative analysis of disulfiram, $C_{10}H_{20}N_2S_4$—the active ingredient in the drug Antabuse—requires that we first convert the sulfur to SO_2 by combustion, and then oxidize the SO_2 to H_2SO_4 by bubbling it through a solution of H_2O_2. When the conversion is complete, the amount of H_2SO_4 is determined by titrating with NaOH.

To convert the moles of NaOH used in the titration to the moles of disulfiram in the sample, we need to know the stoichiometry of each reaction. Writing a balanced reaction for H_2SO_4 and NaOH is straightforward

$$H_2SO_4\,(aq) + 2NaOH\,(aq) \rightarrow 2H_2O\,(l) + Na_2SO_4\,(aq)$$
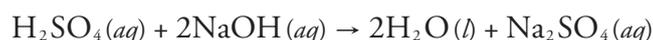
but the balanced reactions for the oxidations of $C_{10}H_{20}N_2S_4$ to SO_2, and of SO_2 to H_2SO_4 are not as immediately obvious. Although we can balance these redox reactions, it is often easier to deduce the overall stoichiometry by use a little chemical logic.
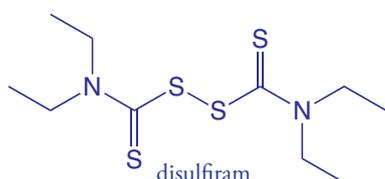
disulfiram

Example 2.7

An analysis for disulfiram, $C_{10}H_{20}N_2S_4$, in Antabuse is carried out by oxidizing the sulfur to H_2SO_4 and titrating the H_2SO_4 with NaOH. If a 0.4613-g sample of Antabuse requires 34.85 mL of 0.02500 M NaOH to titrate the H_2SO_4, what is the %w/w disulfiram in the sample?

SOLUTION

Calculating the moles of H_2SO_4 is easy—first, we calculate the moles of NaOH used in the titration

$$(0.02500 \text{ M}) \times (0.03485 \text{ L}) = 8.712\mathbf{5} \times 10^{-4} \text{ mol NaOH}$$

and then we use the titration reaction's stoichiometry to calculate the corresponding moles of H_2SO_4.

$$8.172\mathbf{5} \times 10^{-4} \text{ molNaOH} \times \frac{1 \text{ mol } H_2SO_4}{2 \text{ mol NaOH}} = 4.356\mathbf{2} \times 10^{-4} \text{ mol } H_2SO_4$$

Here is where we use a little chemical logic. Instead of balancing the reactions for the combustion of $C_{10}H_{20}N_2S_4$ to SO_2 and for the subsequent oxidation of SO_2 to H_2SO_4, we recognize that a conservation of mass requires that all the sulfur in $C_{10}H_{20}N_2S_4$ ends up in the H_2SO_4; thus

$$4.356\mathbf{2} \times 10^{-4} \text{ mol } H_2SO_4 \times \frac{1 \text{ mol S}}{\text{mol } H_2SO_4} \times$$

$$\frac{1 \text{ mol } C_{10}H_{20}N_2S_4}{4 \text{ mol S}} = 1.089\mathbf{0} \times 10^{-4} \text{ mol } C_{10}H_{20}N_2S_4$$

$$1.089\mathbf{0} \times 10^{-4} \text{ mol } C_{10}H_{20}N_2S_4 \times$$

$$\frac{296.54 \text{ g } C_{10}H_{20}N_2S_4}{\text{mol } C_{10}H_{20}N_2S_4} = 0.032293 \text{ g } C_{10}H_{20}N_2S_4$$

$$\frac{0.032293 \text{ g } C_{10}H_{20}N_2S_4}{0.4613 \text{ g sample}} \times 100 = 7.000\% \text{ w/w } C_{10}H_{20}N_2S_4$$

The titration reaction is

$$H_2SO_4\,(aq) + 2NaOH\,(aq) \longrightarrow$$
$$2H_2O\,(l) + Na_2SO_4\,(aq)$$
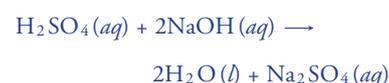
A conservation of mass is the essence of stoichiometry!

2D Basic Equipment

The array of equipment available for making analytical measurements and working with analytical samples is impressive, ranging from the simple and inexpensive, to the complex and expensive. With three exceptions—the measurement of mass, the measurement of volume, and the drying of materials—we will postpone the discussion of equipment to later chapters where its application to specific analytical methods is relevant.

2D.1   Equipment for Measuring Mass

An object's mass is measured using a digital electronic ANALYTICAL BALANCE (Figure 2.3).[2] An electromagnet levitates the sample pan above a permanent cylindrical magnet. When we place an object on the sample pan, it displaces the sample pan downward by a force equal to the product of the sample's mass and its acceleration due to gravity. The balance detects this downward movement and generates a counterbalancing force by increasing the current to the electromagnet. The current needed to return the balance to its original position is proportional to the object's mass. A typical electronic balance has a capacity of 100–200 g, and can measure mass to the nearest ±0.01 mg to ±1 mg.

If the sample is not moisture sensitive, a clean and dry container is placed on the balance. The container's mass is called the tare and most balances allow you to set the container's tare to a mass of zero. The sample is transferred to the container, the new mass is measured and the sample's mass determined by subtracting the tare. A sample that absorbs moisture from the air is treated differently. The sample is placed in a covered weighing bottle and their combined mass is determined. A portion of the sample is removed and the weighing bottle and the remaining sample are reweighed. The difference between the two masses gives the sample's mass.

Several important precautions help to minimize errors when we determine an object's mass. To minimize the effect of vibrations, the balance is placed on a stable surface and in a level position. Because the sensitivity of an analytical balance is sufficient to measure the mass of a fingerprint, materials often are handled using tongs or laboratory tissues. Volatile liquid samples must be weighed in a covered container to avoid the loss of sample by evaporation. To minimize fluctuations in mass due to air currents, the balance pan often is housed within a wind shield, as seen in Figure 2.3. A sample that is cooler or warmer than the surrounding air will create a convective air currents that affects the measurement of its mass. For this reason, bring your samples to room temperature before determining their mass. Finally, samples dried in an oven are stored in a desiccator to prevent them from reabsorbing moisture from the atmosphere.

2D.2   Equipment for Measuring Volume

Analytical chemists use a variety of glassware to measure volume, including graduated cylinders, volumetric pipets, and volumetric flasks. The choice of what type of glassware to use depends on how accurately and how precisely we need to know the sample's volume and whether we are interested in containing or delivering the sample.

Although we tend to use interchangeably, the terms "weight" and "mass," there is an important distinction between them. Mass is the absolute amount of matter in an object, measured in grams. Weight, W, is a measure of the gravitational force, g, acting on that mass, m:

$$W = m \times g$$

An object has a fixed mass but its weight depends upon the acceleration due to gravity, which varies subtly from location-to-location.

A balance measures an object's weight, not its mass. Because weight and mass are proportional to each other, we can calibrate a balance using a standard weight whose mass is traceable to the standard prototype for the kilogram. A properly calibrated balance gives an accurate value for an object's mass; see Appendix 9 for more details on calibrating a balance.

Figure 2.3 The photo shows a typical digital electronic balance capable of determining mass to the nearest ±0.1 mg. The sticker inside the balance's wind shield is its annual calibration certification.

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2   For a review of other types of electronic balances, see Schoonover, R. M. *Anal. Chem.* **1982**, *54*, 973A-980A.

A GRADUATED CYLINDER is the simplest device for delivering a known volume of a liquid reagent (Figure 2.4). The graduated scale allows you to deliver any volume up to the cylinder's maximum. Typical accuracy is ±1% of the maximum volume. A 100-mL graduated cylinder, for example, is accurate to ±1 mL.

A VOLUMETRIC PIPET provides a more accurate method for delivering a known volume of solution. Several different styles of pipets are available, two of which are shown in Figure 2.5. Transfer pipets provide the most accurate means for delivering a known volume of solution. A transfer pipet delivering less than 100 mL generally is accurate to the hundredth of a mL. Larger transfer pipets are accurate to a tenth of a mL. For example, the 10-mL transfer pipet in Figure 2.5 will deliver 10.00 mL with an accuracy of ±0.02 mL.

To fill a transfer pipet, use a rubber suction bulb to pull the solution up past the calibration mark (*Never use your mouth to suck a solution into a pipet!*). After replacing the bulb with your finger, adjust the solution's level to the calibration mark and dry the outside of the pipet with a laboratory tissue. Allow the pipet's contents to drain into the receiving container with the pipet's tip touching the inner wall of the container. A small portion of the liquid remains in the pipet's tip and is not be blown out. With some measuring pipets any solution remaining in the tip must be blown out.

Delivering microliter volumes of liquids is not possible using transfer or measuring pipets. Digital micropipets (Figure 2.6), which come in a variety of volume ranges, provide for the routine measurement of microliter volumes.

Graduated cylinders and pipets deliver a known volume of solution. A VOLUMETRIC FLASK, on the other hand, contains a specific volume of solution (Figure 2.7). When filled to its calibration mark, a volumetric flask that contains less than 100 mL generally is accurate to the hundredth of a mL, whereas larger volumetric flasks are accurate to the tenth of a mL. For
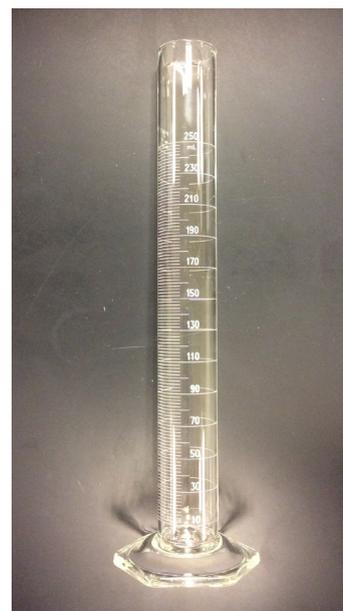
Figure 2.4 An example of a 250-mL graduated cylinder.

Figure 2.6 A set of two digital micropipets. The pipet on the left deliver volumes between 0.5 µL and 10 µL and the pipet on the right delivers volumes between 10 µL and 100 µL.

calibration mark

Figure 2.5 Two examples of 10-mL volumetric pipets. The pipet on the top is a transfer pipet and the pipet on the bottom is a Mohr measuring pipet. The transfer pipet delivers a single volume of 10.00 mL when filled to its calibration mark. The Mohr pipet has a mark every 0.1 mL, allowing for the delivery of variable volumes. It also has additional graduations at 11 mL, 12 mL, and 12.5 mL.

Figure 2.7 A collection of volumetric flasks with volumes of 10 mL, 50 mL, 100, mL, 250 mL, and 500 mL.

Figure 2.8 Close-up of the 10-mL transfer pipet from Figure 2.5.

A volumetric flask has similar markings, but uses the abbreviation T. C. for "to contain" in place of T. D.

example, a 10-mL volumetric flask contains 10.00 mL±0.02 mL and a 250-mL volumetric flask contains 250.0 mL±0.12 mL.

Because a volumetric flask contains a solution, it is used to prepare a solution with an accurately known concentration. Transfer the reagent to the volumetric flask and add enough solvent to bring the reagent into solution. Continuing adding solvent in several portions, mixing thoroughly after each addition, and then adjust the volume to the flask's calibration mark using a dropper. Finally, complete the mixing process by inverting and shaking the flask at least 10 times.

If you look closely at a volumetric pipet or a volumetric flask you will see markings similar to those shown in Figure 2.8. The text of the markings, which reads

$$10 \text{ mL T. D. at } 20 \text{ }^{\circ}\text{C} \pm 0.02 \text{ mL}$$

indicates that the pipet is calibrated to deliver (T. D.) 10 mL of solution with an uncertainty of ±0.02 mL at a temperature of 20 $^{\circ}$C. The temperature is important because glass expands and contracts with changes in temperatures; thus, the pipet's accuracy is less than ±0.02 mL at a higher or a lower temperature. For a more accurate result, you can calibrate your volumetric glassware at the temperature you are working by weighing the amount of water contained or delivered and calculating the volume using its temperature dependent density.

You should take three additional precautions when you work with pipets and volumetric flasks. First, the volume delivered by a pipet or contained by a volumetric flask assumes that the glassware is clean. Dirt and grease on the inner surface prevent liquids from draining evenly, leaving droplets of liquid on the container's walls. For a pipet this means the delivered volume is less than the calibrated volume, while drops of liquid above the calibration mark mean that a volumetric flask contains more than its calibrated volume. Commercially available cleaning solutions are available for cleaning pipets and volumetric flasks.

Second, when filling a pipet or volumetric flask the liquid's level must be set exactly at the calibration mark. The liquid's top surface is curved into a MENISCUS, the bottom of which should align with the glassware's calibration mark (Figure 2.9). When adjusting the meniscus, keep your eye in line with the calibration mark to avoid parallax errors. If your eye level is above the calibration mark you will overfill the pipet or the volumetric flask and you will underfill them if your eye level is below the calibration mark.

Finally, before using a pipet or volumetric flask rinse it with several small portions of the solution whose volume you are measuring. This ensures the removal of any residual liquid remaining in the pipet or volumetric flask.

2D.3   Equipment for Drying Samples

Many materials need to be dried prior to their analysis to remove residual moisture. Depending on the material, heating to a temperature between 110 °C and 140 °C usually is sufficient. Other materials need much higher temperatures to initiate thermal decomposition.

Conventional drying ovens provide maximum temperatures of 160 °C to 325 °C, depending on the model. Some ovens include the ability to circulate heated air, which allows for a more efficient removal of moisture and shorter drying times. Other ovens provide a tight seal for the door, which allows the oven to be evacuated. In some situations a microwave oven can replace a conventional laboratory oven. Higher temperatures, up to as much as 1700 °C, require a muffle furnace (Figure 2.10).

After drying or decomposing a sample, it is cooled to room temperature in a desiccator to prevent the readsorption of moisture. A DESICCATOR (Figure 2.11) is a closed container that isolates the sample from the atmosphere. A drying agent, called a DESICCANT, is placed in the bottom of the container. Typical desiccants include calcium chloride and silica gel. A perforated plate sits above the desiccant, providing a shelf for storing samples. Some desiccators include a stopcock that allows them to be evacuated.

2E   Preparing Solutions

Preparing a solution of known concentration is perhaps the most common activity in any analytical lab. The method for measuring out the solute and the solvent depend on the desired concentration and how exact the solution's concentration needs to be known. Pipets and volumetric flasks are used when we need to know a solution's exact concentration; graduated cylinders, beakers, and/or reagent bottles suffice when a concentrations need
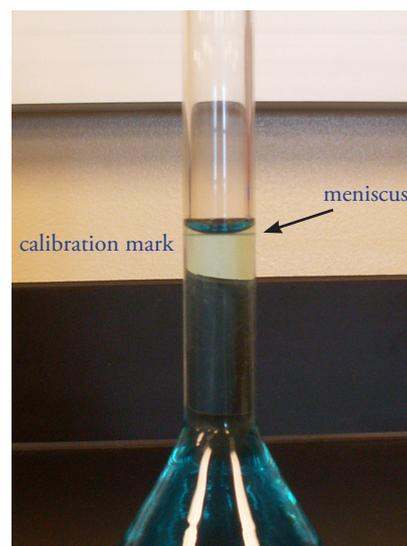

Figure 2.9 Proper position of the solution's meniscus relative to the volumetric flask's calibration mark.

Figure 2.10 Example of a muffle furnace.

Figure 2.11 Example of a desiccator. The solid in the bottom of the desiccator is the desiccant, which in this case is silica gel.

only be approximate. Two methods for preparing solutions are described in this section.

2E.1   Preparing Stock Solutions

A STOCK SOLUTION is prepared by weighing out an appropriate portion of a pure solid or by measuring out an appropriate volume of a pure liquid, placing it in a suitable flask, and diluting to a known volume. Exactly how one measure's the reagent depends on the desired concentration unit. For example, to prepare a solution with a known molarity you weigh out an appropriate mass of the reagent, dissolve it in a portion of solvent, and bring it to the desired volume. To prepare a solution where the solute's concentration is a volume percent, you measure out an appropriate volume of solute and add sufficient solvent to obtain the desired total volume.

Example 2.8

Describe how to prepare the following three solutions: (a) 500 mL of approximately 0.20 M NaOH using solid NaOH; (b) 1 L of 150.0 ppm Cu^{2+} using Cu metal; and (c) 2 L of 4% v/v acetic acid using concentrated glacial acetic acid (99.8% w/w acetic acid).

SOLUTION

(a) Because the desired concentration is known to two significant figures, we do not need to measure precisely the mass of NaOH or the volume of solution. The desired mass of NaOH is

$$\frac{0.20 \text{ mol NaOH}}{L} \times \frac{40.0 \text{ g NaOH}}{\text{mol NaOH}} \times 0.50 \text{ L} = 4.0 \text{ g}$$

To prepare the solution, place 4.0 grams of NaOH, weighed to the nearest tenth of a gram, in a bottle or beaker and add approximately 500 mL of water.

(b) Since the desired concentration of Cu^{2+} is given to four significant figures, we must measure precisely the mass of Cu metal and the final solution volume. The desired mass of Cu metal is

$$\frac{150.0 \text{ mg Cu}}{L} \times 1.000 \text{ L} \times \frac{1 \text{ g}}{1000 \text{ mg}} = 0.1500 \text{ g Cu}$$

To prepare the solution, measure out exactly 0.1500 g of Cu into a small beaker and dissolve it using a small portion of concentrated HNO_3. To ensure a complete transfer of Cu^{2+} from the beaker to the volumetric flask—what we call a QUANTITATIVE TRANSFER—rinse the beaker several times with small portions of water, adding each rinse to the volumetric flask. Finally, add additional water to the volumetric flask's calibration mark.

(c) The concentration of this solution is only approximate so it is not necessary to measure exactly the volumes, nor is it necessary to account for the fact that glacial acetic acid is slightly less than 100% w/w acetic acid (it is approximately 99.8% w/w). The necessary volume of glacial acetic acid is

$$\frac{4 \text{ mL CH}_3\text{COOH}}{100 \text{ mL}} \times 2000 \text{ mL} = 80 \text{ mL CH}_3\text{COOH}$$

To prepare the solution, use a graduated cylinder to transfer 80 mL of glacial acetic acid to a container that holds approximately 2 L and add sufficient water to bring the solution to the desired volume.

Practice Exercise 2.5

Provide instructions for preparing 500 mL of 0.1250 M $KBrO_3$.

Click here to review your answer to this exercise.

2E.2   Preparing Solutions by Dilution

Solutions are often prepared by diluting a more concentrated stock solution. A known volume of the stock solution is transferred to a new container and brought to a new volume. Since the total amount of solute is the same before and after DILUTION, we know that

$$C_o \times V_o = C_d \times V_d \qquad\qquad 2.2$$

where C_o is the stock solution's concentration, V_o is the volume of stock solution being diluted, C_d is the dilute solution's concentration, and V_d is the volume of the dilute solution. Again, the type of glassware used to measure V_o and V_d depends on how precisely we need to know the solution's concentration.

Note that equation 2.2 applies only to those concentration units that are expressed in terms of the solution's volume, including molarity, formality, normality, volume percent, and weight-to-volume percent. It also applies to weight percent, parts per million, and parts per billion if the solution's density is 1.00 g/mL. We cannot use equation 2.2 if we express concentration in terms of molality as this is based on the mass of solvent, not the volume of solution. See Rodríquez-López, M.; Carrasquillo, A. *J. Chem. Educ.* **2005**, *82*, 1327-1328 for further discussion.

Example 2.9

A laboratory procedure calls for 250 mL of an approximately 0.10 M solution of NH_3. Describe how you would prepare this solution using a stock solution of concentrated NH_3 (14.8 M).

SOLUTION

Substituting known volumes into equation 2.2

$$14.8 \text{ M} \times V_o = 0.10 \text{ M} \times 250 \text{ mL}$$

and solving for V_o gives 1.7 mL. Since we are making a solution that is approximately 0.10 M NH_3, we can use a graduated cylinder to measure the 1.7 mL of concentrated NH_3, transfer the NH_3 to a beaker, and add sufficient water to give a total volume of approximately 250 mL.

Although we express molarity as mol/L, we can express the volumes in mL if we do so both for V_o and for V_d.

Practice Exercise 2.6

To prepare a standard solution of Zn^{2+} you dissolve a 1.004 g sample of Zn wire in a minimal amount of HCl and dilute to volume in a 500-mL volumetric flask. If you dilute 2.000 mL of this stock solution to 250.0 mL, what is the concentration of Zn^{2+}, in μg/mL, in your standard solution?

Click here to review your answer to this exercise.

As shown in the following example, we can use equation 2.2 to calculate a solution's original concentration using its known concentration after dilution.

Example 2.10

A sample of an ore was analyzed for Cu^{2+} as follows. A 1.25 gram sample of the ore was dissolved in acid and diluted to volume in a 250-mL volumetric flask. A 20 mL portion of the resulting solution was transferred by pipet to a 50-mL volumetric flask and diluted to volume. An analysis of this solution gives the concentration of Cu^{2+} as 4.62 μg/L. What is the weight percent of Cu in the original ore?

SOLUTION

Substituting known volumes (with significant figures appropriate for pipets and volumetric flasks) into equation 2.2

$$(C_{Cu})_o \times 20.00 \text{ mL} = 4.62 \text{ μg/L } Cu^{2+} \times 50.00 \text{ mL}$$

and solving for $(C_{Cu})_o$ gives the original concentration as 11.55 μg/L Cu^{2+}. To calculate the grams of Cu^{2+} we multiply this concentration by the total volume

$$\frac{11.55 \text{ μg } Cu^{2+}}{\text{mL}} \times 250.0 \text{ mL} \times \frac{1 \text{ g}}{10^6 \text{ μg}} = 2.888 \times 10^{-3} \text{ g } Cu^{2+}$$

The weight percent Cu is

$$\frac{2.888 \times 10^{-3} \text{ g } Cu^{2+}}{1.25 \text{ g sample}} \times 100 = 0.231\% \text{ w/w } Cu^{2+}$$

2F   Spreadsheets and Computational Software

If you do not have access to Microsoft Excel or another commercial spreadsheet package, you might considering using Calc, a freely available open-source spreadsheet that is part of the OpenOffice.org software package at www.openoffice.org.

Analytical chemistry is an quantitative discipline. Whether you are completing a statistical analysis, trying to optimize experimental conditions, or exploring how a change in pH affects a compound's solubility, the ability to work with complex mathematical equations is essential. Spreadsheets, such as Microsoft Excel are an important tool for analyzing your data and for

preparing graphs of your results. Scattered throughout this textbook you will find instructions for using spreadsheets.

Although spreadsheets are useful, they are not always well suited for working with scientific data. If you plan to pursue a career in chemistry, you may wish to familiarize yourself with a more sophisticated computational software package, such as the freely available open-source program that goes by the name R, or commercial programs such as Mathematica or Matlab. You will find instructions for using R scattered throughout this textbook.

Despite the power of spreadsheets and computational programs, *don't forget that the most important software is behind your eyes and between your ears*. The ability to think intuitively about chemistry is a critically important skill. In many cases you will find that it is possible to determine if an analytical method is feasible or to approximate the optimum conditions for an analytical method without resorting to complex calculations. Why spend time developing a complex spreadsheet or writing software code when a "back-of-the-envelope" estimate will do the trick? Once you know the general solution to your problem, you can use a spreadsheet or a computational program to work out the specifics. Throughout this textbook we will introduce tools to help develop your ability to think intuitively.

You can download the current version of R from www.r-project.org. Click on the link for Download: CRAN and find a local mirror site. Click on the link for the mirror site and then use the link for Linux, MacOS X, or Windows under the heading "Download and Install R."

For an interesting take on the importance of intuitive thinking, see *Are You Smart Enough to Work at Google?* by William Poundstone (Little, Brown and Company, New York, 2012).

2G   The Laboratory Notebook

Finally, we can not end a chapter on the basic tools of analytical chemistry without mentioning the laboratory notebook. A laboratory notebook is your most important tool when working in the lab. If kept properly, you should be able to look back at your laboratory notebook several years from now and reconstruct the experiments on which you worked.

Your instructor will provide you with detailed instructions on how he or she wants you to maintain your notebook. Of course, you should expect to bring your notebook to the lab. Everything you do, measure, or observe while working in the lab should be recorded in your notebook as it takes place. Preparing data tables to organize your data will help ensure that you record the data you need, and that you can find the data when it is time to calculate and analyze your results. Writing a narrative to accompany your data will help you remember what you did, why you did it, and why you thought it was significant. Reserve space for your calculations, for analyzing your data, and for interpreting your results. Take your notebook with you when you do research in the library.

Maintaining a laboratory notebook may seem like a great deal of effort, but if you do it well you will have a permanent record of your work. Scientists working in academic, industrial and governmental research labs rely on their notebooks to provide a written record of their work. Questions about research carried out at some time in the past can be answered by finding the appropriate pages in the laboratory notebook. A laboratory

notebook is also a legal document that helps establish patent rights and proof of discovery.

2H   Key Terms

analytical balance	concentration	desiccant
desiccator	dilution	formality
graduated cylinder	meniscus	molality
molarity	normality	parts per million
parts per billion	p-function	quantitative transfer
scientific notation	significant figures	SI units
stock solution	volume percent	volumetric flask
volumetric pipet	weight percent	weight-to-volume percent

2I   Chapter Summary

There are a few basic numerical and experimental tools with which you must be familiar. Fundamental measurements in analytical chemistry, such as mass, use base SI units, such as the kilogram. Other units, such as energy, are defined in terms of these base units. When reporting a measurement, we must be careful to include only those digits that are significant, and to maintain the uncertainty implied by these significant figures when transforming measurements into results.

The relative amount of a constituent in a sample is expressed as a concentration. There are many ways to express concentration, the most common of which are molarity, weight percent, volume percent, weight-to-volume percent, parts per million and parts per billion. Concentrations also can be expressed using p-functions.

Stoichiometric relationships and calculations are important in many quantitative analyses. The stoichiometry between the reactants and the products of a chemical reaction are given by the coefficients of a balanced chemical reaction.

Balances, volumetric flasks, pipets, and ovens are standard pieces of equipment that you will use routinely in the analytical lab. You should be familiar with the proper way to use this equipment. You also should be familiar with how to prepare a stock solution of known concentration, and how to prepare a dilute solution from a stock solution.

2J   Problems

1. Indicate how many significant figures are in each of the following numbers.

   a. 903   b. 0.903   c. 1.0903
   d. 0.0903   e. 0.09030   f. 9.03×10^2

2. Round each of the following to three significant figures.

    a. 0.89377   b. 0.89328   c. 0.89350
    d. 0.8997   e. 0.08907

3. Round each to the stated number of significant figures.

    a. the atomic weight of carbon to 4 significant figures
    b. the atomic weight of oxygen to 3 significant figures
    c. Avogadro's number to 4 significant figures
    d. Faraday's constant to 3 significant figures

4. Report results for the following calculations to the correct number of significant figures.

    a. $4.591 + 0.2309 + 67.1 =$

    b. $313 - 273.15 =$

    c. $712 \times 8.6 =$

    d. $1.43/0.026 =$

    e. $(8.314 \times 298)/96\,485 =$

    f. $\log(6.53 \times 10^{-5}) =$

    g. $10^{-7.14} =$

    h. $(6.51 \times 10^{-5}) \times (8.14 \times 10^{-9}) =$

5. A 12.1374 g sample of an ore containing Ni and Co is carried through Fresenius' analytical scheme, as shown in Figure 1.1. At point A the combined mass of Ni and Co is 0.2306 g, while at point B the mass of Co is 0.0813 g. Report the weight percent Ni in the ore to the correct number of significant figures.

6. Figure 1.2 shows an analytical method for the analysis of Ni in ores based on the precipitation of Ni^{2+} using dimethylglyoxime. The formula for the precipitate is $Ni(C_4H_7N_2O_2)_2$. Calculate the precipitate's formula weight to the correct number of significant figures.

7. An analyst wishes to add 256 mg of Cl^- to a reaction mixture. How many mL of 0.217 M $BaCl_2$ is this?

8. The concentration of lead in an industrial waste stream is 0.28 ppm. What is its molar concentration?

9. Commercially available concentrated hydrochloric acid is 37.0% w/w HCl. Its density is 1.18 g/mL. Using this information calculate (a) the molarity of concentrated HCl, and (b) the mass and volume, in mL, of a solution that contains 0.315 moles of HCl.

10. The density of concentrated ammonia, which is 28.0% w/w NH_3, is 0.899 g/mL. What volume of this reagent should you dilute to 1.0×10^3 mL to make a solution that is 0.036 M in NH_3?

11. A 250.0 mL aqueous solution contains 45.1 μg of a pesticide. Express the pesticide's concentration in weight-to-volume percent, in parts per million, and in parts per billion.

12. A city's water supply is fluoridated by adding NaF. The desired concentration of F^- is 1.6 ppm. How many mg of NaF should you add per gallon of treated water if the water supply already is 0.2 ppm in F^-?

13. What is the pH of a solution for which the concentration of H^+ is 6.92×10^{-6} M? What is the $[H^+]$ in a solution whose pH is 8.923?

14. When using a graduate cylinder, the absolute accuracy with which you can deliver a given volume is ±1% of the cylinder's maximum volume. What are the absolute and the relative uncertainties if you deliver 15 mL of a reagent using a 25 mL graduated cylinder? Repeat for a 50 mL graduated cylinder.

15. Calculate the molarity of a potassium dichromate solution prepared by placing 9.67 grams of $K_2Cr_2O_7$ in a 100-mL volumetric flask, dissolving, and diluting to the calibration mark.

16. For each of the following explain how you would prepare 1.0 L of a solution that is 0.10 M in K^+. Repeat for concentrations of 1.0×10^2 ppm K^+ and 1.0% w/v K^+.

    a. KCl   b. K_2SO_4 c. $K_3Fe(CN)_6$

This is an example of a serial dilution, which is a useful method for preparing very dilute solutions of reagents.

17. A series of dilute NaCl solutions are prepared starting with an initial stock solution of 0.100 M NaCl. Solution A is prepared by pipeting 10 mL of the stock solution into a 250-mL volumetric flask and diluting to volume. Solution B is prepared by pipeting 25 mL of solution A into a 100-mL volumetric flask and diluting to volume. Solution C is prepared by pipeting 20 mL of solution B into a 500-mL volumetric flask and diluting to volume. What is the molar concentration of NaCl in solutions A, B and C?

18. Calculate the molar concentration of NaCl, to the correct number of significant figures, if 1.917 g of NaCl is placed in a beaker and dissolved in 50 mL of water measured with a graduated cylinder. If this solution is quantitatively transferred to a 250-mL volumetric flask and diluted to volume, what is its concentration to the correct number of significant figures?

19. What is the molar concentration of NO_3^- in a solution prepared by mixing 50.0 mL of 0.050 M KNO_3 with 40.0 mL of 0.075 M $NaNO_3$? What is pNO_3 for the mixture?

20. What is the molar concentration of Cl^- in a solution prepared by mixing 25.0 mL of 0.025 M NaCl with 35.0 mL of 0.050 M $BaCl_2$? What is pCl for the mixture?

21. To determine the concentration of ethanol in cognac a 5.00 mL sample of the cognac is diluted to 0.500 L. Analysis of the diluted cognac gives an ethanol concentration of 0.0844 M. What is the molar concentration of ethanol in the undiluted cognac?

2K Solutions to Practice Exercises

Practice Exercise 2.1

The correct answer to this exercise is 1.9×10^{-2}. To see why this is correct, let's work through the problem in a series of steps. Here is the original problem

$$\frac{0.250 \times (9.93 \times 10^{-3}) - 0.100 \times (1.927 \times 10^{-2})}{9.93 \times 10^{-3} + 1.927 \times 10^{-2}} =$$

Following the correct order of operations we first complete the two multiplications in the numerator. In each case the answer has three significant figures, although we retain an extra digit, highlight in **red**, to avoid round-off errors.

$$\frac{2.482 \times 10^{-3} - 1.927 \times 10^{-3}}{9.93 \times 10^{-3} + 1.927 \times 10^{-2}} =$$

Completing the subtraction in the numerator leaves us with two significant figures since the last significant digit for each value is in the hundredths place.

$$\frac{0.555 \times 10^{-3}}{9.93 \times 10^{-3} + 1.927 \times 10^{-2}} =$$

The two values in the denominator have different exponents. Because we are adding together these values, we first rewrite them using a common exponent.

$$\frac{0.555 \times 10^{-3}}{0.993 \times 10^{-2} + 1.927 \times 10^{-2}} =$$

The sum in the denominator has four significant figures since each of the addends has three decimal places.

$$\frac{0.555 \times 10^{-3}}{2.920 \times 10^{-2}} =$$

Finally, we complete the division, which leaves us with a result having two significant figures.

$$\frac{0.55\mathbf{5} \times 10^{-3}}{2.92\mathbf{0} \times 10^{-2}} = 1.9 \times 10^{-2}$$

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Practice Exercise 2.2

The concentrations of the two solutions are

$$\frac{0.50 \text{ mol NaCl}}{\text{L}} \times \frac{58.44 \text{ g NaCl}}{\text{mol NaCl}} \times$$

$$\frac{10^6 \text{ μg}}{\text{g}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2.9 \times 10^4 \text{ μg/mL NaCl}$$

$$\frac{0.25 \text{ mol SrCl}_2}{\text{L}} \times \frac{158.5 \text{ g SrCl}_2}{\text{mol SrCl}_2} \times$$

$$\frac{10^6 \text{ μg}}{\text{g}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 4.0 \times 10^4 \text{ μg/mL SrCl}_2$$

The solution of $SrCl_2$ has the larger concentration when it is expressed in μg/mL instead of in mol/L.

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Practice Exercise 2.3

The concentrations of Na^+ and SO_4^{2-} are

$$\frac{1.5 \text{ g Na}_2\text{SO}_4}{0.500 \text{ L}} \times \frac{1 \text{ mol Na}_2\text{SO}_4}{142.0 \text{ g Na}_2\text{SO}_4} \times$$

$$\frac{2 \text{ mol Na}^+}{\text{mol Na}_2\text{SO}_4} = 4.2\mathbf{3} \times 10^{-2} \text{ M Na}^+$$

$$\frac{1.5 \text{ g Na}_2\text{SO}_4}{0.500 \text{ L}} \times \frac{1 \text{ mol Na}_2\text{SO}_4}{142.0 \text{ g Na}_2\text{SO}_4} \times$$

$$\frac{1 \text{ mol SO}_4^{2-}}{\text{mol Na}_2\text{SO}_4} = 2.1\mathbf{1} \times 10^{-2} \text{ M SO}_4^{2-}$$

The pN and pSO_4 values are

$$pK = -\log(4.2\mathbf{3} \times 10^{-2}) = 1.37$$

$$pSO_4 = -\log(2.1\mathbf{1} \times 10^{-2}) = 1.68$$

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Practice Exercise 2.4

First, we find the moles of AgBr

$$0.250 \text{ g AgBr} \times \frac{1 \text{ mol AgBr}}{187.8 \text{ g AgBr}} = 1.33\mathbf{1} \times 10^{-3} \text{ mol AgBr}$$

and then the moles and volume of $Na_2S_2O_3$

$$1.33\mathbf{1} \times 10^{-3} \text{ mol AgBr} \times \frac{2 \text{ mol Na}_2\text{S}_2\text{O}_3}{\text{mol AgBr}} =$$

$$2.662 \times 10^{-3} \text{ mol Na}_2\text{S}_2\text{O}_3$$

$$2.66\mathbf{2} \times 10^{-3} \text{ mol Na}_2\text{S}_2\text{O}_3 \times$$

$$\frac{1 \text{ L}}{0.0138 \text{ mol Na}_2\text{S}_2\text{O}_3} \times \frac{1000 \text{ mL}}{\text{L}} = 193 \text{ mL}$$

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Practice Exercise 2.5

Preparing 500 mL of 0.1250 M KBrO_3 requires

$$0.5000 \text{ L} \times \frac{0.1250 \text{ mol KBrO}_3}{\text{L}} \times \frac{167.00 \text{ g KBrO}_3}{\text{mol KBrO}_3} = 10.44 \text{ g KBrO}_3$$

Because the concentration has four significant figures, we must prepare the solution using volumetric glassware. Place a 10.44 g sample of KBrO_3 in a 500-mL volumetric flask and fill part way with water. Swirl to dissolve the KBrO_3 and then dilute with water to the flask's calibration mark.

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Practice Exercise 2.6

The first solution is a stock solution, which we then dilute to prepare the standard solution. The concentration of Zn^{2+} in the stock solution is

$$\frac{1.004 \text{ g Zn}^{2+}}{500.0 \text{ mL}} \times \frac{10^6 \text{ μg}}{\text{g}} = 2008 \text{ μg Zn}^{2+}/\text{ml}$$

To find the concentration of the standard solution we use equation 2.2

$$\frac{2008 \text{ μg Zn}^{2+}}{\text{mL}} \times 2.000 \text{ mL} = C_d \times 250.0 \text{ mL}$$

where C_d is the standard solution's concentration. Solving gives a concentration of 16.06 μg Zn^{2+}/mL.

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