IGERT
GeoChem R-01

CHAPTER 2

Concentration Units

2.1 INTRODUCTION

Use of the correct and consistent units is key to solving problems in the sciences and engineering. Environmental engineers and scientists often are interested in the concentrations of chemical species. Thus, you must decide which of the many possible sets of concentration units makes sense for a given application.

concentration: the quantity of the material per volume (or mass) of the surrounding environment

Concentration refers to the quantity of the material per volume or mass of the surrounding environment. There are many measures of the quantity of material in the environment and thus many different concentration units. Some concentration units make chemical sense, whereas others persist because they are perceived to be more convenient or have the inertia of common use behind them.

In this chapter, the rules for tracking units through calculations will be reviewed. Common units of concentration for chemical species in the environment will be discussed in Section 2.2. The common molar, mass, and dimensionless concentration units for dissolved species are reviewed in Sections 2.3, 2.4, and 2.5, respectively. Equivalents units are introduced in Section 2.6. In Section 2.7, a table for interconverting units is presented. Common units for gas phase and solid phase species are investigated in Section 2.8 and 2.9, respectively. In Section 2.10, the concept of activity is introduced.

The focus of this chapter is on *concentration units*. Units are the currency by which amounts of the material and volumes of the surroundings are quantified. In addition to units, you also may choose between several *concentration scales*. Concentration scales have their own standard states and will be discussed more thoroughly in Section 3.7.2. Common concentration scales are molarity, molality, and mole fraction.

2.2 UNITS ANALYSIS

The tracking or accounting system for units is called *units analysis*. The rules of units analysis are simple:

- Addition and subtraction
  Add or subtract only terms with identical units.

- Multiplication, division, and raising to a power

  When multiplying or dividing terms (or raising terms to a power), also multiply or divide (or raised to a power) the units associated with the terms.

- Other functions

  Most other common mathematical functions (e.g., logarithms, exponentiation, and the trigonometric functions) can operate only on terms with no units (i.e., *unitless* or *dimensionless* terms). In other words, the arguments of logarithmic, exponential, and trigonometric functions must be dimensionless.

Units are associated with each value you calculate. However, you can manipulate units independent of values. For example, you can use units alone to find conversion factors between units (see Example 2.1).

.3 MOLAR CONCENTRATION UNITS

xample 2.1: **Units Conversion**

ow do you convert the concen-ıtion units of milligrams per er (mg/L) to the concentration ıits of moles per liter (mol/L)?

ılution:

ı answer this question, you do ıt require values. In fact, you ı not even need to know what ɜ words milligrams and moles ɜan. Simply treat the units as ɪms in an equation:

$$(mg/L)(X) = (mol/L)$$

ılving for X: X = mol/mg

ıus, to convert from mg/L to ɔl/L, **multiply by the number moles per milligram.**

ıle (abbr. ***mol***): one mole is ɔ22×10²³ atoms, molecules, or ɪs

2.3.1 Introduction

Environmental chemistry often concerns the *combinations* of chemical species to form other species. Thus, it makes sense to choose concentration units that reflect *the proportions in which chemicals combine*. One logical choice of units is the number of atoms, molecules, or ions of a given substance per volume (or mass) of the system. After all, if one H^+ ion combines with one OH^- ion to form one H_2O molecule, why not express each concentration in units of the number of ions (or molecules) per liter? This choice of units makes great chemical sense. However, it is unwieldy because the numbers of atoms, molecules, and ions are so large. For example, 1 milliliter of water contains about 3×10^{22} molecules of water. (To put this large number in perspective, 3×10^{22} cans of soft drink would fill the world's oceans eight times over.) If you chose the *number per liter* concentration units, then the concentrations of the major ions in seawater are $[Na^+] = 2.82\times10^{23}$ ions/L and $[Cl^-] = 3.28\times10^{23}$ ions/L; not very practical numbers. (Note: As usual, denote the concentration of A by [A].)

2.3.2 The mole

You can create a more practical system of concentration units by assigning a name to a large, but arbitrary, number of atoms. The name ***mole*** (abbreviation: mol) has been assigned to 6.022×10^{23} atoms, molecules, or ions. The number 6.022×10^{23} is called *Avogadro's number*. The value of Avogadro's number is arbitrary and evolved through a tortuous history (see the *Historical Note* at the end of this chapter). The concentration units based on the mole are called ***molar units***, typically in moles/L (abbreviated M, with mM = millimoles per liter and μM = micromoles per liter).

molar units: concentration units of moles per liter (1 molar = 1 M = 1 mol/L)

Thoughtful Pause

What are the sodium and chloride ion concentrations in seawater in units of moles per liter?

The major ions in seawater in molar units are

$$[Na^+] = (2.82\times10^{23}\text{ ions/L})/(6.022\times10^{23}\text{ ions/mol})$$
$$= 0.468\text{ mol/L} = 0.468\text{ M, and:}$$

$$[Cl^-] = (3.28\times10^{23}\text{ ions/L})/(6.022\times10^{23}\text{ ions/mol})$$
$$= 0.545\text{ mol/L} = 0.545\text{ M}$$

Key idea: Molar units are proportional to the number of atoms, molecules, or ions in a given volume

It is important to remember that molar units are *proportional to the number of atoms, molecules, or ions in a given volume*. The proportionality constant relating the number of atoms (or molecules or ions) to the number of moles is the same for every substance.

Thoughtful Pause

In molar units, what is the constant relating moles to the number of atoms, molecules, or ions and what are the units of this constant?

Key idea: Molar units are the only set of concentration units with the same constant relating the concentration units to the number of atoms, molecules, or ions for all chemical species

Key idea: Unless otherwise stated, always use molar units in equilibrium calculations for dissolved species concentrations

In molar units, the constant relating moles to numbers is Avogadro's number (6.022×10^{23} atoms, molecules, or ions per mole). The molar system is the only set of concentration units with the *same constant relating the concentration units to the number of atoms, molecules, or ions for all chemical species*. Another way to express this idea is to take the approach of Example 2.1. For any set of concentration units, you can write (something/L)(X) = (number/L). Molar units (where: something = moles) is the only set of concentration units where X is constant for all chemical species.

To summarize, molar units are the only concentration units with the same constant relating the concentration units to the number of atoms, molecules, or ions for all chemical species. Thus, molar units are especially useful in equilibrium calculations, where combining ratios are critical. You should *always use molar units in equilibrium calculations* for the concentrations of dissolved species.

2.3.3 Molarity

As will be discussed in the *Historical Note*, Avogadro's number was set by defining the mass of 1 mole of the ^{12}C isotope of carbon atoms equal to exactly 12 grams. (The ^{12}C isotope of carbon has 6 neutrons in addition to

6 protons and 6 electrons.) With Avogadro's number fixed, you can use the combining ratios of the elements to calculate the mass of 1 mole of each element. The mass of 1 mole of an element (i.e., the mass of 6.022×10^{23} atoms of an element) is called its ***atomic weight***. The ***molecular weight*** of a molecule is calculated by summing the atomic weights of each atom in the molecule (or ion) multiplied by the number of times the atom occurs in the molecule or ion. The number of times the atom occurs is called its ***stoichiometric coefficient*** in the molecule or ion. The concept of stoichiometry (from the Greek *stoicheion* element + *metrein* to measure) shall be used throughout this text. The molecular weight† of a molecule or ion containing n different atoms is given by $\sum_{i=1}^{n} \nu_{ij} AW_i$, where ν_{ij} = stoichiometric coefficient of atom i in molecule (or ion) j, and AW_i = atomic weight of atom i.

omic weight: the mass of 1 ole of an element

olecular weight: the mass of 1 ole of a molecule or ion

oichiometric coefficient: here, e number of occurrences of an om in a molecule or ion

am molecular weight: molecular weight in grams per mole

The calculation of molecular weight is illustrated in Example 2.2. In the older literature, the term ***gram molecular weight*** is used to refer to the molecular weight expressed in grams (or, more properly, g/mol). Thus, the statements "The molecular weight of water is 18 g/mol" and "The gram molecular weight of water is 18 g/mol" are identical.

***ample 2.2:* Calculation of olecular Weight**

hat is the molecular weight of rrous ammonium sulfate?

lution:

e molecular formula is $Fe(NH_4)_2(SO_4)_2$. One mole ntains 1 mole of Fe, 2 moles N, 2 moles of S, 8 moles of , and 8 moles of H. The mocular weight is

$$
\begin{aligned}
W &= 1(AW_{Fe}) + 2(AW_N) + 2(AW_S) + 8(AW_O) + 8(AW_H) \\
&= 1(55.85 \text{ g/mol}) + 2(14.01 \text{ g/mol}) + 2(32.06 \text{ g/mol}) + 8(16.00 \text{ g/mol}) + 8(1.01 \text{ g/mol}) \\
&= 284.07 \text{ g/mol}
\end{aligned}
$$

e molecular weight of $Fe(NH_4)_2(SO_4)_2$ is 284.07 mol.

2.3.4 Analytical concentrations and formality

In some applications, molar units may seem inappropriate. For example, how would you make up a 1 M NaCl solution? When NaCl is added to water, it dissociates nearly completely to Na^+ and Cl^- ions (see Section 1.4.2). Thus, although you might add 1 mole (about 58.44 g) of NaCl molecules to 1 liter of water, the actual number of moles of NaCl molecules in solution after a short period of time is quite small. The basic question is: Does a 1 M NaCl solution contain 1 M of NaCl molecules *before* any chemical reactions occur or *after* chemical reactions occur?

The most common terminology in environmental applications is to label solutions by the number of moles per liter of starting material *added*, regardless of the final composition of the mixture. For example, a solution made up by diluting 1 mole of HCl to 1 L of water shall be referred to as a 1 M HCl solution (even though the actual HCl concentration at equilibrium is only about 1×10^{-3} M††). The number of moles per liter of starting material added sometimes is called the ***analytical concentration***.

alytical concentration: number of moles of starting material ded per liter of water

In the older literature, a solution obtained by adding 1 mole of NaCl molecules to 1 L of water was called a 1 formal (or 1 F) NaCl solution. The use of *formal concentration units* (or *formality*) is uncommon in environmental applications and will not be used again in this text.

† The term *molecular weight* is commonly used to refer to the mass per mole of ions as well as molecules. More precisely, you can use the term *formula weight* to indicate the mass of any species per mole of that species. The formula weight uses the stoichiometry given in the chemical formula of the species.

†† After Chapter 7, you will be able to calculate the equilibrium HCl concentration.

2.3.5 Molality

Another potential problem with molar concentrations is that they depend on the temperature and pressure of the system. Why? Molar concentrations depend on temperature and pressure because the *solution volume depends on temperature and pressure.*† You can create a temperature- and pressure-independent concentration scale by dividing the number of moles of material by the solvent *mass* rather than the solvent *volume*. The resulting concentration units are called the ***molal concentration units***:

molal concentration units: concentration units of moles per kg of solvent (1 molal = 1 m = 1 mol/kg solvent)

1 molal (abbreviated 1 m or 1 *m*) = 1 mol/kg of solvent

The difference between the molar and molal scales is small for dilute aqueous solutions near 25°C and 1 atm of pressure. To convert units:

mol/L solution = (mol/kg solvent)(kg solvent/L solution)
= (mol/kg solvent)(kg solvent/kg solution)(kg solution/L solution)

Thus:

molarity = (molality)(kg solvent/kg solution)ρ

where ρ = density of the solution in kg/L. For aqueous solutions, the solvent is pure water.

Thoughtful Pause

Why is the difference between molar and molal units small for dilute aqueous solutions at room temperature and pressure?

For *dilute* aqueous solutions, the mass of the dissolved species is small and 1 kg of solution contains very close to 1 kg of water. In addition, near 25°C and 1 atm of pressure, the density of *dilute* solutions is near 1 kg/L. Thus:

molarity = (molality)(kg solvent/kg solution)ρ
= (molality)($\approx$ 1 kg solvent/kg solution)($\approx$ 1 kg solution/L solution)
$\approx$ molality

An example of conversion between molality and molarity is shown in Example 2.3.

Example 2.3: **Conversion of Molal and Molar Units**

What is the molarity of a 1 m NaCl solution (at 25°C and 1 atm)?

Solution:
From the text:
molarity = (molality)(kg solvent/kg solution)ρ

For a 1 m NaCl solution: mass of solvent = 1 kg water, mass of solution = mass of water + mass of solute = 1.05844 kg, and ρ = 1.0405 kg/L (at 25°C and 1 atm).

Thus, 1 M NaCl = (1 m)(1 kg/1.05844 kg)(1.0405 kg/L) = **0.98 M**.

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† By way of justification, assume for a moment that dilute aqueous species behave like ideal gases. The ideal gas law states that (pressure)(volume) = (constant)(number of moles)(temperature); see Section 2.8. In other words, the molar concentration (= number of moles/volume) is proportional to the ratio of the pressure and temperature. Thus, molar concentrations vary with temperature and pressure.

2.4 MASS CONCENTRATION UNITS

2.4.1 Introduction

The amount of material added to the environment typically is quantified by its mass. As a result, mass concentration units are very common. Typical units are milligrams per liter (= 10^{-3} g/L = mg/L), micrograms per liter (= 10^{-6} g/L = μg/L), and nanograms per liter (= 10^{-9} g/L = ng/L).

Units analysis reveals that you should multiply molar concentration (in mol/L) by the molecular weight (MW, in g/mol) to convert to the mass scale (in g/L) (see also Example 2.1):

Key idea: The conversion factor relating mass and molar units is the molecular weight: concentration in g/L = (MW in g/mol)(concentration in mol/L)

$$\text{concentration in g/L} = (\text{MW in g/mol})(\text{concentration in mol/L})$$

The conversion factor relating mass and molar units is the molecular weight. Thus, the conversion factor between mass units and the number of atoms (or moles) is *different* for every substance having a different molecular weight.

This observation leads to two problems with mass units. First, mass concentration units do not give you the combining proportions directly. For example, 1 mole of silver ions (Ag^-) reacts with 1 mole of chloride ions (Cl^-) to form silver chloride. One mole of silver ions also can react with 1 mole of bromide ions (Br^-) to form silver bromide. In molar units, the 1:1 stoichiometry between silver and chloride or silver and bromide is clear. In mass units, a solution containing 1 mg/L of Ag^- requires 0.33 mg/L of Cl^- or 0.74 mg/L of Br^- to satisfy the 1:1 stoichiometry. Thus, the combining proportion is not obvious when concentrations are expressed in mass units. Another example of conversion between molar stoichiometry and mass units is given in Example 2.4.

Example 2.4: **Stoichiometry in Mass Units (AgI Example)**

What mass concentration of iodide ions is required to react with 1 mg/L silver ions if Ag^+ and I^- react with 1:1 stoichiometry?

Solution:
1 mg/L Ag^- = 1×10^{-3} g Ag^+/L = (1×10^{-3} g Ag^-/L)/(107.868 g Ag/mol Ag) = 9.27×10^{-6} M Ag^+

This is equivalent to (9.27×10^{-6} mol I^-/L)(126.905 g I^-/mol I^-) = 1.18×10^{-3} g/L or **1.18 mg/L.**

Second, mass concentration units are difficult to compare. For example, you may wish to verify that a 1 mg/L solution of nitrite (NO_2^-) contains *more* nitrogen than a 1 mg/L solution of nitrate (NO_3^-) (see Example 2.5).

2.4.2 Mass concentrations as other species

To allow for comparison of mass concentration units, the concentrations of related species sometimes are calculated by using the *molecular weight of a common species*. If the common species is Y, you say that the concentration of species X is "1 mg/L as Y" or "1 mg Y/L" or "1 mg X-Y/L." *This notation means that you are using the molecular weight of Y for the molecular weight of X.* For example, the concentration of the 1 mg/L NO_2^- solution discussed above can be expressed in terms of mg/L as N (see Example 2.5). You write that the solution concentration is "0.30 mg/L NO_2^- as N" or "0.30 mg N/L" or "0.30 mg NO_2^--N/L." In doing so, you are using that the molecular weight of atomic nitrogen (14 g/mol) for the molecular weight of nitrate.

When expressing the concentration as another species, it is useful to first convert the mass concentration to molar units, then multiply by the molecular weight of the *as* species. For example, suppose the personnel at a wastewater treatment plant wish to determine if the measured effluent ammonium (NH_4^+) concentration of 2.3 mg/L NH_4^+ violates the discharge limit of 1.8 mg NH_4^+-N/L. The ammonium concentration is

$$[NH_4^-] = (2.3 \text{ mg/L } NH_4^+)(10^{-3} \text{ g/mg})/(17 \text{ g } NH_4^-/\text{mol } NH_4^+)$$
$$= 1.4\times10^{-4} \text{ mol/L } NH_4^+$$

This is equivalent to $(1.4\times10^{-4} \text{ mol/L } NH_4^+)(14 \text{ g N/mol N})(10^3 \text{ mg/g}) = 2.0$ mg NH_4^--N/L; in violation of the discharge limit. See also Example 2.6.

In performing these calculations, be sure to account for stoichiometry; that is, the number of times the *as* fragment appears in the original substance. For example, suppose 25 mg/L of alum ($Al_2(SO_4)_3\cdot18H_2O$) is added at a drinking water treatment plant. What is the alum dose expressed as Al? The alum dose is:

$$\text{dose} = (25 \text{ mg alum/L})(10^{-3} \text{ g/mg})/(666.43 \text{ g alum/mol alum})$$
$$= 3.75\times10^{-5} \text{ mol alum/L}$$

There are 2 moles of Al per mole of alum. Thus, the dose is:

$$\text{dose} = (2 \text{ mol Al/mol alum})(3.75\times10^{-5} \text{ mol alum/L})$$
$$= 7.50\times10^{-5} \text{ mole Al/L, or:}$$
$$= (7.50\times10^{-5} \text{ mol Al/L})(26.98 \text{ g Al/mol})(10^3 \text{ mg/g})$$
$$= 2.02 \text{ mg/L as Al}$$

Another example is shown in Example 2.7. To summarize the procedure for converting a concentration in mg X/L into mg Y/L:

$$\text{concentration in mg as Y/L} =$$
$$(\text{concentration in mg X/L})(\text{mol Y/mol X})(\text{MW Y})/(\text{MW X})$$

Why use the *mass as* notation? The advantage of expressing mass concentrations as other species is that species concentrations can be compared easily. If a natural water is said to contain 0.5 mg/L NO_3^- and 0.2 mg/L NH_4^-, it is difficult to see at first that ammonium is the larger source of nitrogen. However, when you express the nitrate and ammonium concentrations *in the same units* (i.e., 0.11 mg/L NO_3^- as N and 0.16 mg/L NH_4^+ as N; please verify these values), it becomes clear that ammonium is the larger nitrogen source. In a similar fashion, economists may express currencies in common units (euros or U.S. dollars) to compare prices in different countries.

***Example 2.5:* Stoichiometry in Mass Units (Nitrogen Example)**

What is the nitrogen content of a 1 mg/L nitrite solution and a 1 mg/L nitrate solution?

Solution:
1 mg/L NO_2^- = [$(1\times10^{-3}$ g NO_2^-/L)/(46 g NO_2^-/mol)](14 g N/mol) = **0.30 mg of N per L**

1 mg/L NO_3^- = [$(1\times10^{-3}$ g NO_3^-/L)/(62 g NO_2^-/mol)](14 g N/mol) = **0.23 mg of N per L**

***Example 2.6:* Mass Concentrations as Another Species**

A rinse water from an electroplating bath has a chromate (CrO_4^{2-}) concentration of 10 mg/L. What is the chromate concentration expressed as Cr?

Solution:
The bath is
(10 mg/L)(10^{-3} g/mg)/(116 g chromate/mol chromate)
= 8.62×10^{-5} M chromate
Expressed as Cr, the concentration is
(8.62×10^{-5} mol chromate/L)(1 mol Cr/mol chromate)(52 g Cr/mol)(1000 mg/g)
= **4.48 mg/L as Cr**

Key idea: Use the *mass as* notation to convert the mass concentrations of several species to the same set of units to compare or add them

***Example 2.7:* Mass Concentrations as Another Species with Stoichiometry Correction**

An industrial waste stream contains 5 mg/L of phenol (C_6H_6O). The discharge limit for the industry is 3 mg/L total organic carbon (TOC). TOC is the mass concentration of carbon from organic compounds. Does the waste stream meet the discharge limit?

Solution:
The molecular weight of phenol is:

$$(6\ \text{C})(12\ \text{g/mol C}) + (6\ \text{H})(1\ \text{g/mol H}) + (1\ \text{O})(16\ \text{g/mol O}) = 94\ \text{g/mol}$$

The phenol concentration is:

$$[\text{phenol}] = (5\ \text{mg/L})(10^{-3}\ \text{g/mg})/(94\ \text{g phenol/mol phenol}) = 5.32\times10^{-5}\ \text{mol/L}$$

There are 6 moles of C per mole of phenol. Thus, the TOC concentration is:

$$(6\ \text{mol C/mol phenol})\times(5.32\times10^{-5}\ \text{M phenol}) = 3.19\times10^{-4}\ \text{mole C/L}$$

Or:

$$= (3.19\times10^{-4}\ \text{mol C/L})(12\ \text{g C/mol})(1000\ \text{mg/g}) = 3.8\ \text{mg/L as C}$$

The TOC is 3.8 mg/L, exceeding the discharge permit.

Key idea: When adding species concentrations in mass units, convert all concentrations to the same units by expressing each value as a common species (exceptions: TDS and salinity)

The *mass as* notation is particularly useful for compounds that are measured as a group because it allows you to express the concentration of two different species by using the same mass units. Recall from Section 2.2 that you can add or subtract only terms with the same units. Thus, the *mass as* approach allows you to add and subtract species concentrations when using mass units. For example, you may wish to know how much of the total soluble cyanide in a waste stream is present as the species cyanide (CN^-) and how much is present as cadmium cyanide (assuming for the moment that cyanide and cadmium cyanide are the only forms of cyanide in the waste). Some common cyanide measurement methods measure the *sum* of the two species. Expressing the total soluble cyanide as CN eliminates any confusion introduced by the difference in molecular weights between cyanide and cadmium cyanide. Thus, if the CN^- concentration was 1.1 mg/L as CN and the cadmium cyanide concentration was 4.2 mg/L as CN, the total cyanide concentration can be calculated as 1.1 mg CN/L + 4.2 mg CN/L = 5.3 mg/L as CN.

Before leaving the *mass as* notation, please note that the stoichiometry is not always clear from inspection. As an example of the confusion in stoichiometry, consider the case of chlorine. Species containing *active chlorine* (usually meaning chlorine in the +I oxidation state) often are expressed in units of mg/L as Cl_2. The pertinent reactions for several chlorine-containing species of environmental significance are as follows:

$$Cl_2 + H_2O = HOCl + Cl^- + H^+ \qquad \text{eq. 2.1}$$
$$HOCl = OCl^- + H^+ \qquad \text{eq. 2.2}$$
$$HOCl + NH_3 = NH_2Cl + H_2O \qquad \text{eq. 2.3}$$

It is clear from these reactions that 1 mole of HOCl forms from 1 mole of Cl_2 (eq. 2.1), 1 mole of OCl^- forms from 1 mole of HOCl (eq. 2.2), and 1 mole NH_2Cl forms from 1 mole of HOCl (eq. 2.3). Thus, each mole of HOCl, OCl^-, and NH_2Cl is equivalent to 1 mole of Cl_2. As a result: 1 mg/L Cl_2 as Cl_2 = 1 mg/L HOCl as Cl_2 = 1 mg/L OCl^- as Cl_2 = 1 mg/L NH_2Cl as Cl_2.

2.4.3 Unusual mass concentration units

Having stressed that you can add only terms with the same units, it now must be noted that there are a few common water quality parameters where you add species concentrations expressed in *different* mass units. One example is ***total dissolved solids*** (TDS), operationally defined as the mass of material that passes through a specified filtration operation. The TDS is *measured* gravimetrically (i.e., by weight). It also can be *calculated* by adding the masses of the individual components in the water. This approach violates the rules of units analysis because it requires that you add terms with different units. For example, the TDS of a solution containing 30 mg/L Na^+ and 40 mg/L Cl^- is 70 mg/L. The sodium ion and chloride ion

total dissolved solids (***TDS***): sum of the mass concentrations of species passing through a specified filter

concentrations have different units (mg/L as Na^+ and mg/L as Cl^-, respectively). Nonetheless, you add these terms of different units when calculating the TDS from species concentrations.

Another example in which species concentrations with different mass units are added is *salinity*, *S*(‰). The salinity of seawater is related to the sum of the masses of dissolved inorganic species per kg of seawater. Thus, *TDS and salinity are exceptions to the general rule that masses are not additive when expressed in different units.*

2.5 DIMENSIONLESS CONCENTRATION UNITS

It is common to use dimensionless units to express the concentrations of chemical species in the environment. Several examples are illustrated below.

mole fraction: concentration units equal to the number of moles of the substance divided by the total number of moles in the system (dimensionless; mole fraction of A = x_A)

2.5.1 Mole fraction

The ***mole fraction*** is the number of moles of the substance divided by the total number of moles in the system. The total number of moles in the system is the sum of the moles of solvent and moles of all dissolved species, where the solvent is pure water in dilute aqueous solutions. The mole fraction (denoted x) is used frequently in chemical engineering and is useful in some thermodynamic derivations (see Chapter 3).

2.5.2 Parts per X

Pollutant concentrations are frequently expressed in parts per some number of parts. Examples are parts per million (ppm), parts per billion (ppb), and parts per trillion (ppt or pptr). Using the example of ppm, the notation 10 ppm refers to 10 parts of something per million parts of something else. The word *parts* can refer to masses or volumes (denoted, for example, ppm_m and ppm_v, respectively) but typically refers to masses for aqueous or solid systems.

Key idea: Units of ppm and mg/L are nearly identical in dilute aqueous solutions with solution densities near 1.0 kg/L

In dilute aqueous systems at environmentally important temperatures and pressures, the density of water is very close to 1.0 kg/L. Thus, 1 liter of water weighs approximately 1 kg or 10^6 mg. A concentration of 1 mg/L means 1 mg of material in 1 liter of water = 1 mg in 10^6 mg = 1 part in 1 million parts = 1 ppm. For dilute aqueous systems near 25°C and 1 atm, the units mg/L and ppm are nearly identical. Similarly, ppb and μg/L are nearly interchangeable in dilute aqueous systems (near 25°C and 1 atm), as are ppt and ng/L.

In the more general case:

$$\begin{aligned} \text{ppm} &= \text{mg/kg solution} \\ &= (\text{mass concentration in mg/L})/(\text{solution density in kg/L}) \end{aligned}$$

For example, consider a waste stream consisting of 1 mg of lead in 1 L of water (density = 1.0 kg/L at 25°C, 1 atm). The lead concentration is 1 mg/L or (1 mg Pb/L)/(1.0 kg/L) = 1.0 mg Pb/kg = 1 ppm. If 1 mg of lead was placed in 1 L of a 25% sodium chloride solution (density = 1.19 kg/L at 25°C, 1 atm), the solution still would be 1 mg/L. However, in ppm, the lead concentration is:

$$\begin{aligned}[\text{Pb in ppm}] &= (1\text{ mg Pb/L solution})/(1.19\text{ kg solution/L solution})\\ &= 0.84\text{ mg Pb/kg solution}\\ &= 0.84\text{ ppm.}\end{aligned}$$

There are a few caveats to remember when using the parts per something units. First, make sure you know whether the parts are mass or volume. Second, remember that ppm and mg/L (or ppb and μg/L or ppt and ng/L) are nearly identical *only* in dilute solutions when the density of water is very close to 1.0 kg/L.

2.5.3 Percentage

The concentrations of more concentrated solutions are often expressed as a percentage. This dimensionless unit refers to the mass (or volume) of the substance per mass (or volume) of the system. In aqueous solution, the percentage concentration is the mass of the species per mass of solution, expressed as a percentage. Thus:

$$\text{conc. (in \% by mass)} = 10^{-4}\,(\text{conc. in ppm})$$

For dilute aqueous solutions near 25°C and 1 atm:

$$\begin{aligned}\text{conc. (in \% by mass)} &= 10^{-4}\,(\text{conc. in ppm})\\ &\approx 10^{-4}(\text{conc. in mg/L})\end{aligned}$$

Key idea: A 1% mixture is nearly 10,000 mg/L if the olution density is near 1.0 kg/L

In general:

$$\begin{aligned}\text{conc. (in \% by mass)} &= 10^{-4}\,(\text{conc. in ppm})\\ &= 10^{-4}\,(\text{conc. in mg/L})/(\text{density in kg/L})\end{aligned}$$

Thus, a 1% sludge stream is very close to 10,000 mg/L solids if its density is near 1.0 kg/L.

.6 EQUIVALENTS

Another common set of concentration units in aquatic chemistry is equivalents units. The term *equivalents* is confusing at first blush because it appears to carry a different meaning with each use. In fact, converting from molar to equivalents units is trivial. Analogous to Example 2.1, units analysis will reveal how to convert from molar to equivalents units:

$$\text{equivalents/L} = \text{eq/L} = (\text{conversion factor})(\text{mol/L})$$

normality: concentration units in equivalents per liter (1 equivalent/L = 1 eq/L = 1 normal = 1 N)

Thus, the conversion factor that multiplies mol/L to get eq/L must have units of equivalents/mol. A solution containing 1 eq/L is said to be 1 normal (= 1 N). Equivalence concentration units also are called ***normality***.

Now the hard part: *how many equivalents are there per mole*? The answer to this question depends on the context. In acid-base (proton transfer) reactions, *equivalents* generally refers to the number of protons transferred (or capable of being transferred). Thus, a 0.5 M HCl solution is (0.5 mol/L)(1 eq/mol) = 0.5 eq/L = 0.5 N since HCl has 1 proton (i.e., one H^+) available to transfer. The concentration of a 0.5 M H_2SO_4 solution in eq/L is (0.5 mol/L)(2 eq/mole) = 1 eq/L = 1 N since H_2SO_4 has two protons available to transfer.

Similarly, in redox (electron transfer reactions), *equivalents* generally refers to the number of electrons transferred. Thus, a 0.4 mM O_2 solution is: (0.4 mmol/L)(4 eq/mol) = 1.6 meq/L = 1.6 mN, since each molecule of O_2 can accept four electrons to become two molecules of H_2O (formally: $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$; more on redox reactions in Chapter 16).

You also can use equivalents to express species concentrations in terms of important fragments. For example, a 1.2×10^{-5} M $Cu(CN)_3^-$ solution made be said to contain (1.2×10^{-5} mol/L)(3 eq of cyanide/mol) = 3.6×10^{-5} eq/L of cyanide.

Key idea: When using equivalents units, always ask "Equivalent to what?"

As can been seen by these examples, there are many uses of equivalents units. It is critical to know the basis of comparison. *When using equivalents units, always ask, "Equivalent to what?"*

2.7 REVIEW OF UNITS INTERCONVERSION

The conversion factors for changing from one set of units to another are listed in Table 2.1. Remember that each conversion factor has units.

2.8 COMMON CONCENTRATION UNITS IN THE GAS PHASE

Gas phase concentrations usually are expressed in the partial pressure scale. Thus, the concentration of a gas is defined as its partial pressure, P_i, where P_i = pressure exerted by the gas/total pressure. The most common unit in aquatic chemistry for expressing the concentration of a gas is the *atmosphere* (atm).† Other concentration units for trace air pollutants are mass concentration (typically μg/m^3), parts per *X* (especially ppm$_v$ = parts by volume per million parts by volume), and percentage units. Gas concentration units are dependent on pressure and temperature.

† The formal (Système International d'Unités, or SI) unit of pressure is the pascal (abbreviated Pa), where 1 Pa = 1 N/m^2. One atmosphere is 101,325 Pa or 101.325 kPa. One bar of pressure is 100,000 Pa or 0.9869 atm.

Table 2.2: Interconversion Factors for Concentration Units in Aqueous Systems
[Multiply units in row by table entry to get units in the column.
Example: To convert mol/L to mg/L, multiply by (1000)(molecular weight)]

	Molar (mol/L = M)	Mole fraction (x)	Mass (mg/L)	Mass (mg/L as Y)	Parts per million (ppm_m)	Percentage (mass basis)
Molar (mol/L = M)	1	$\frac{1}{T}$	1000(MW)	$1000(MW_Y)$	$\frac{1000(MW)}{\rho}$	$\frac{10^{-4}(1000)(MW)}{\rho}$
Mole fraction (x)	T	1	1000(MW)(T)	$1000(MW_Y)(T)$	$\frac{1000(MW)(T)}{\rho}$	$\frac{10^{-4}(1000)(MW)(T)}{\rho}$
Mass (mg/L)	$\frac{1}{1000(MW)}$	$\frac{1}{1000(MW)(T)}$	1	$\frac{MW_Y}{MW}$	$\frac{1}{\rho}$	$\frac{10^{-4}}{\rho}$
Mass (mg/L as Y)	$\frac{1}{1000(MW_Y)}$	$\frac{1}{1000(MW_Y)(T)}$	$\frac{MW}{MW_Y}$	1	$\frac{MW}{(MW_Y)\rho}$	$\frac{10^{-4}(MW)}{(MW_Y)\rho}$
Parts per million (ppm_m)	$\frac{\rho}{1000(MW)}$	$\frac{\rho}{1000(MW)(T)}$	ρ	$\frac{(\rho)MW_Y}{MW}$	1	10^{-4}
Percentage (mass basis)	$\frac{10^4\rho}{1000(MW)}$	$\frac{10^4\rho}{1000(MW)(T)}$	$10^4\rho$	$\frac{(10^4\rho)MW_Y}{MW}$	10^4	1

Notes: MW = molecular weight of species of interest (g/mol)
T = total mol/L in solution, including the solvent
ρ = solution density (kg/L)
MW_Y = molecular weight of Y (g/mol)
The number 1000 has units of mg/g

The concentration unit ppm_v is defined for a gas as:

$$= \frac{10^6\left(\frac{\text{moles of species}}{\text{volume}}\right)}{\frac{\text{moles of air}}{\text{volume}}}$$

The ideal gas law states that:

$$PV = nRT$$

where P = pressure, V = volume, n = number of moles of gas, R = ideal gas constant, and T = absolute temperature (°K). Thus: moles of air per unit volume = $n/V = P/RT$. In addition, the number of moles of a species per unit volume is given by:

$$\text{number of moles per volume} = 10^{-6}(\text{conc. in } \mu\text{g/m}^3)/\text{MW}$$

Substituting:

$$\text{concentration (ppm}_v = \frac{RT}{P}\left(\frac{\text{concentration in } \mu\text{g/m}^3}{\text{MW}}\right)$$

2.9 COMMON CONCENTRATION UNITS IN THE SOLID PHASE

In solid environments (e.g., soils, sludges, sediments, and other sorbents), common mass concentration units are mg/kg (i.e., milligrams of pollutant per kilogram of solid), parts per X (i.e., parts per million), and percentages. As with aqueous systems, the units of ppm and mg/kg are equivalent: 1 ppm = 1 mg/kg. For equilibrium calculations, the concentration of a pure solid phase is given by the mole fraction.

2.10 ACTIVITY

In the first Section of this chapter, concentration was defined as the quantity of the material per volume or mass of the surrounding environment. Now you might ask: Is mass or molar concentration the *best* measure of how a substance actually *behaves* in the environment? When seeking to describe the behavior of substances in the environment, mass or molar concentration may not be the most appropriate indicator.

To understand the limitations on concentration, consider the problem of determining the behavior of a group of children in a swimming pool. One might start by counting the children. Say there are 20 children in a small pool of volume 15 m^3. Is the number concentration (also called the *bather load*, which equals 20 per 15 m^3 = 1.3×10^{-3}/L) the best measure of the sprightliness of the children?

Thoughtful Pause

What factors (besides the number per volume) affect the liveliness of the children?

The activity of the children may depend on several factors other than their number concentration. For example, the children may be less active if the water temperature is cooler. Also, the activity of the children may change if adults are present in the pool.

Similarly, chemical species may behave differently under different environmental conditions, *even at the same mass or molar concentration*. As with the children in the pool, the behavior of chemical species depends on the water temperature and concentration of other species. In addition, the system pressure may influence the way in which chemical species behave.

As an example, consider three glasses of water, each with the same small amount of salt dissolved in the water. One glass is at room temperature, one at elevated temperature, and one at room temperature with a lot of Epsom salts (a form of $MgSO_4$) also dissolved in the water. The mass (and molar) concentrations of sodium and chloride ions will be the same for each glass. However, the ions will be *more active* in the warmer water and *less active* with the Epsom salts than in the first glass. The ions are less active in the presence of Epsom salts because the sodium ions interact electrostatically with sulfate ions and the chloride ions interact electrostatically with the magnesium ions. This is analogous to the children in the pool: the children may be less active (i.e., less rambunctious) if they are interacting with the adults in the pool.

Scientists have recognized for nearly 100 years that temperature, pressure, and the presence of other chemical species affect the behavior of dissolved chemicals in water. As a result, it has been necessary to develop a new approach in quantifying the amount of material in a system. This approach is an idealized concentration (sometimes called, in the older literature, a *thermodynamic concentration*), which takes into account the effects of temperature, pressure, and the presence of other chemical species on the behavior of dissolved chemicals. The idealized concentration is called ***activity***. The activity of species A is denoted as $\{A\}$.

activity: an idealized concentration, used in thermodynamic calculations, which takes into account the effects of temperature, pressure, and the presence of other chemical species on the behavior of dissolved chemicals

Activity is the proper way to express the quantity of species in thermodynamic calculations. As you shall see in Chapter 3, equilibrium is a thermodynamic concept. Thus, you *should* use activity (and *not* concentration) as the sole indicator of species quantity. However, you shall find that activity and concentration are nearly identical in dilute solutions (where the concentrations of other chemical species are small) at near standard temperature and pressure. In other words, the conversion factor relating activity and concentration (called the *activity coefficient*) is nearly 1 in dilute solution near 25°C and 1 atm of pressure.

In this text, the effects of other inert chemical species will be ignored for most of the book, and molar concentration units will be used. In Chapter 3, activity will be used in developing thermodynamic relationships. In Chapter 21, a detailed analysis will be made of the effects of other species on activity.

2.11 SUMMARY

Units are key to engineering and science calculations, and concentration units are critical when manipulating chemical species concentrations. In equilibrium calculations, molar units (mol/L = M) are useful because they capture the combining proportions inherent in chemical reactions. In other cases, you may wish to express mass concentrations in the same units so they can be added. Thus, concentrations sometimes are expressed as some other species. In expressing the concentration of species X as Y, use the molecular weight of Y as the molecular weight of X and take into account the number of moles of Y per mole of X. Dimensionless concentration units (mole fraction; parts per million, billion, or trillion; and percentages) also are in common use. For aqueous system with a density near 1 kg/L, 1 part per million (1 ppm) is very close to 1 mg/L.

Another way to use the same units (or currency) when writing concentrations is to use units of normality (or equivalence/L). In this case, always ask yourself: Equivalent to what? In other words, the *basis of the equivalence* (i.e., the number of equivalence per mole) must be established clearly. Common equivalences are the number of H^+ or electrons accepted or donated. Gas phase and solid phase concentration units also were reviewed in this chapter.

Mass or molar concentration units may not be the most appropriate way to describe the *behavior* of chemical species in solution. In particular, temperature, pressure, and the presence of other chemical species are known to affect the behavior of dissolved chemicals. This observation necessitates a new look at concentration and has lead to the development of an *idealized concentration* called *activity*. Activity is the most appropriate choice of expressing the quantity of material in thermodynamic calculations. In this text, the effects of other inert chemicals, temperature, and pressure on the behavior of selected chemical species will be ignored until Chapter 21.

2.12 PART I CASE STUDY: CAN METHYLMERCURY BE FORMED CHEMICALLY IN WATER?

In Chapter 1, four species were identified as being important in determining whether methylmercury can be formed at significant concentrations from the reaction of dissolved methane and Hg^{2+} in water. The four species are CH_3Hg^-, Hg^{2-}, CH_4(aq), and CH_4(g). Based on the lessons of this chapter, it should be possible to select units for the four species in the chemical system.