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 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

**Example 2.1: Units Conversion**

How do you convert the concentration units of milligrams per liter (mg/L) to the concentration units of moles per liter (mol/L)?

**Solution:**
To answer this question, you do not require values. In fact, you need not even know what the words milligrams and moles mean. Simply treat the units as unknowns in an equation:

\[(\text{mg/L}) \times (X) = (\text{mol/L})\]

Solving for \(X\): \(X = \text{mol/mg}\)

Thus, to convert from mg/L to mol/L, multiply by the number of moles per milligram.

**Note** (abbr. mol): one mole is \(6.022 \times 10^{23}\) atoms, molecules, or}

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\(_2\)O 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 \(3 \times 10^{22}\) molecules of water. (To put this large number in perspective, \(3 \times 10^{22}\) cans of soft drink would fill the world's oceans eight times over.) If you choose the number per liter concentration units, then the concentrations of the major ions in seawater are \([\text{Na}^+] = 2.82 \times 10^{22}\) ions/L and \([\text{Cl}^-] = 3.28 \times 10^{22}\) 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 \(6.022 \times 10^{23}\) atoms, molecules, or ions.

The number \(6.022 \times 10^{23}\) 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 mol/L (abbreviated M, with mM = millimoles per liter and uM = 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

\[
[\text{Na}^+] = \frac{(2.82 \times 10^{22} \text{ ions/L})}{(6.022 \times 10^{23} \text{ ions/mol})} = 0.468 \text{ mol/L} = 0.468 \text{ M}, \text{ and:}
\]

\[
[\text{Cl}^-] = \frac{(3.28 \times 10^{23} \text{ ions/L})}{(6.022 \times 10^{23} \text{ ions/mol})} = 0.545 \text{ mol/L} = 0.545 \text{ M}
\]

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?

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}\text{C} isotope of carbon atoms equal to exactly 12 grams. (The ^{12}\text{C} isotope of carbon has 6 neutrons in addition to
omic weight: the mass of 1 mole of an element

molecular weight: the mass of 1 mole of a molecule or ion

stoichiometric coefficient: here, the number of occurrences of an ion in a molecule or ion

mm molecular weight: molecular weight in grams per mole

Example 2.2: Calculation of Molecular Weight

What is the molecular weight of tris ammonium sulfate?

Solution:
The molecular formula is \( (NH_4)_3(SO_4)_2 \). One molecule contains 3 moles of Fe, 2 moles of N, 2 moles of S, 8 moles of O, and 8 moles of H. The molecular weight is

\[
W = 3(AW_{NH_4}) + 2(AW_{SO_4}) + 8(AW_O) + 8(AW_H)
\]

\[
= 3(14.01 \text{ g/mol}) + 2(32.06 \text{ g/mol}) + 8(16.00 \text{ g/mol}) + 8(1.01 \text{ g/mol})
\]

\[
= 284.07 \text{ g/mol}
\]

The molecular weight of \( (NH_4)_3(SO_4)_2 \) is 284.07 mol.

Analytical concentration: number of moles of starting material added per liter of water

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 \( 6.022 \times 10^{23} \) 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 + merein to measure) shall be used throughout this text. The molecular weight \( ^{\dagger} \) of a molecule or ion containing \( n \) different atoms is given by \( \sum_{i=1}^{n} v_i A W_i \), where \( v_i = \text{stoichiometric coefficient of atom } i \) in molecule (or ion) \( j \), and \( A W_i = \text{atomic weight of atom } i \).

The calculation of molecular weight is illustrated in Example 2.2. In the older literature, the term gramm 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.

2.3.4 Analytical concentrations and formalities

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 \( 1 \times 10^{-2} \text{ M} \)). The number of moles per liter of starting material added sometimes is called the analytical concentration.

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 formalities) is uncommon in environmental applications and will not be used again in this text.

\({^\dagger}\) 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.

\( ^{\dagger} \) 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.¹ 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:

\[ 1 \text{ molal (abbreviated } 1 \text{ m or } 1 \text{ m}) = 1 \text{ mol/kg of solvent} \]

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:

\[
\begin{align*}
\text{mol/L solution} &= (\text{mol/kg solvent})(\text{kg solvent/L solution}) \\
&= (\text{mol/kg solvent})(\text{kg solute/kg solution})(\text{kg solution/L solution})
\end{align*}
\]

Thus:

\[ \text{molality} = (\text{molality})(\text{kg solvent/kg solution})\rho \]

where \( \rho \) = density of the solution in kg/L. For aqueous solutions, the solvent is pure water.

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**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:

\[
\begin{align*}
\text{molarity} &= (\text{molality})(\text{kg solvent/kg solution})\rho \\
&= (\text{molality})(1 \text{ kg solvent/kg solution})(1 \text{ kg solution/L solution}) \\
&= \text{molality}
\end{align*}
\]

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

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¹ By way of justification, assume for a moment that dilute aqueous species behave like ideal gases. The ideal gas law states that \((\text{pressure})(\text{volume}) = (\text{constant})(\text{number of moles})(\text{temperature})\); see Section 2.8. In other words, the molar concentration \((= \text{number of moles/volume})\) 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):

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

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 ($\text{Ag}^+$) reacts with 1 mole of chloride ions ($\text{Cl}^-$) to form silver chloride. One mole of silver ions also can react with 1 mole of bromide ions ($\text{Br}^-$) 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 $\text{Ag}^+$ requires 0.33 mg/L of $\text{Cl}^-$ or 0.74 mg/L of $\text{Br}^-$ 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.

Second, mass concentration units are difficult to compare. For example, you may wish to verify that a 1 mg/L solution of nitrite ($\text{NO}_2^-$) contains more nitrogen than a 1 mg/L solution of nitrate ($\text{NO}_3^-$) (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.
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:

\[
1 \text{ mg/L NO}_2^- = \left(1 \times 10^{-3} \text{ g NO}_2^- / \text{L} \right) \times \left(46 \text{ g NO}_2^- / \text{mol} \right) \times \left(14 \text{ g N/mol} \right) = 0.30 \text{ mg of N per L}
\]

\[
1 \text{ mg/L NO}_3^- = \left(1 \times 10^{-3} \text{ g NO}_3^- / \text{L} \right) \times \left(62 \text{ g NO}_3^- / \text{mol} \right) \times \left(14 \text{ g N/mol} \right) = 0.23 \text{ mg of N per L}
\]

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

\[
(10 \text{ mg/L}) \times \left(10^{-3} \text{ g/mg} \right) \times \left(116 \text{ g chromate/mol chromate} \right) = 8.62 \times 10^{-2} \text{ M chromate}
\]

Expressed as Cr, the concentration is

\[
(8.62 \times 10^{-2} \text{ mol chromate/L}) \times \left(1 \text{ mol Cr/mol chromate} \right) 
\times \left(52 \text{ g Cr/mol} \right) \times \left(1000 \text{ mg/g} \right) = 4.48 \text{ mg/L as Cr}
\]

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.

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

\[
[\text{NH}_4^+] = \frac{(2.3 \text{ mg/L NH}_4^+)(10^{-3} \text{ g/mg})}{(17 \text{ g NH}_4^+/\text{mol NH}_4^+)} = 1.4 \times 10^{-4} \text{ mol/L NH}_4^+
\]

This is equivalent to \((1.4 \times 10^{-4} \text{ mol/L NH}_4^+)(14 \text{ g N/mol N})(10^3 \text{ mg/g}) = 2.0 \text{ mg NH}_4^+\)-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\(_2\)O) is added at a drinking water treatment plant. What is the alum dose expressed as Al? The alum dose is:

\[
\text{dose} = \frac{(25 \text{ mg alum/L})(10^{-3} \text{ g/mg})}{(66.453 \text{ g alum/mol alum})} = 3.75 \times 10^{-5} \text{ mol alum/L}
\]

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

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

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

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

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 2.7: Mass Concentrations as Another Species with Stoichiometry Correction

An industrial waste stream contains 5 mg/L of phenol (C₆H₅O). 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:

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

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

\[
(6 \text{ mol C/mole phenol})\times(3.32\times10^{-8} \text{ M phenol}) = 3.19\times10^{-7} \text{ mole C/L}
\]

Or:

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

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 +1 oxidation state) often are expressed in units of mg/L as Cl₂. The pertinent reactions for several chlorine-containing species of environmental significance are as follows:

\[
\begin{align*}
\text{Cl}_2 + \text{H}_2\text{O} & = \text{HOCl} + \text{Cl}^- + \text{H}^+ \quad \text{eq. 2.1} \\
\text{HOCl} & = \text{OCl}^- + \text{H}^+ \quad \text{eq. 2.2} \\
\text{HOCl} + \text{NH}_3 & = \text{NH}_2\text{Cl} + \text{H}_2\text{O} \quad \text{eq. 2.3}
\end{align*}
\]

It is clear from these reactions that 1 mole of HOCl forms from 1 mole of Cl₂ (eq. 2.1), 1 mole of OCl⁻ forms from 1 mole of HOCI (eq. 2.2), and 1 mole NH₂Cl forms from 1 mole of HOCl (eq. 2.3). Thus, each mole of HOCl, OCl⁻, and NH₂Cl is equivalent to 1 mole of Cl₂. As a result: 1 mg/L Cl₂ as Cl₂ = 1 mg/L HOCl = 1 mg/L OCl⁻ = 1 mg/L NH₂Cl as Cl₂.

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.

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, ppmw and ppmv, respectively) but typically refers to masses for aqueous or solid systems.

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 10⁶ mg. A concentration of 1 mg/L means 1 mg of material in 1 liter of water = 1 mg in 10⁶ 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:

\[
\text{ppm} = \frac{\text{mass concentration in mg/L}}{\text{solution density in kg/L}}
\]

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 \((1 \text{ mg Pb/L})/(1.0 \text{ kg/L}) = 1.0 \text{ mg Pb/kg} = 1 \text{ ppm}\). 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:

\[
[\text{Pb in ppm}] = \frac{(1 \text{ mg Pb/L solution})}{(1.19 \text{ kg solution/L solution})} = \frac{0.84 \text{ mg Pb/kg solution}}{1.19} = 0.71 \text{ ppm}.
\]

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 \(\mu\)g/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:

\[
\text{conc. (in \% by mass)} = 10^{-4} \cdot (\text{conc. in ppm})
\]

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

\[
\text{conc. (in \% by mass)} = 10^{-4} \cdot (\text{conc. in ppm}) = 10^{-4} \cdot (\text{conc. in mg/L})
\]

In general:

\[
\text{conc. (in \% by mass)} = 10^{-4} \cdot (\text{conc. in ppm}) = 10^{-4} \cdot (\text{conc. in mg/L})/\text{(density in kg/L)}
\]

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

### 2.6 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:
equivalents/L = eq/L = (conversion factor)(mol/L)

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 H₂SO₄ solution in eq/L is (0.5 mol/L)(2 eq/mole) = 1 eq/L = 1 N since H₂SO₄ 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 O₂ solution is: (0.4 mmol/L)(4 eq/mol) = 1.6 mcq/L = 1.6 mN, since each molecule of O₂ can accept four electrons to become two molecules of H₂O (formally: O₂ - 4e⁻ + 4H⁺ ⟷ 2H₂O; 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)₄⁻ solution made to be said to contain (1.2×10⁻⁵ mol/L)(3 eq of cyanide/mol) = 3.6×10⁻⁵ eq/L of cyanide.

As can be 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, Pᵢ, where Pᵢ = 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/m³), parts per X (especially ppm, = 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/m². 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)]

<table>
<thead>
<tr>
<th></th>
<th>Molar (mol/L = M)</th>
<th>Mole fraction (x)</th>
<th>Mass (mg/L)</th>
<th>Mass (mg/L as Y)</th>
<th>Parts per million (ppmₐ)</th>
<th>Percentage (mass basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar (mol/L = M)</td>
<td>1</td>
<td>(\frac{1}{T})</td>
<td>1000(MW)</td>
<td>1000(MWₐ)</td>
<td>(\frac{1000(MW)}{\rho}) (\times 10^4) (\frac{1000(MW)}{\rho})</td>
<td></td>
</tr>
<tr>
<td>Mole fraction (x)</td>
<td>T</td>
<td>1</td>
<td>1000(MW)(T)</td>
<td>1000(MWₐ)(T)</td>
<td>(\frac{1000(MW)(T)}{\rho}) (\times 10^4) (\frac{1000(MW)(T)}{\rho})</td>
<td></td>
</tr>
<tr>
<td>Mass (mg/L)</td>
<td>(\frac{1}{1000(MW)})</td>
<td>(\frac{1}{1000(MW)(T)})</td>
<td>(\frac{1}{MWₐ})</td>
<td>(\frac{1}{MWₐ}) (\times 10^{-5}) (\frac{1}{MWₐ})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass (mg/L as Y)</td>
<td>(\frac{MW}{1000(MWₐ)})</td>
<td>(\frac{MW}{1000(MWₐ)(T)})</td>
<td>(\frac{MW}{MWₐ})</td>
<td>(\frac{MW}{MWₐ}) (\times 10^{-4}) (\frac{MW}{MWₐ})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parts per million (ppmₐ)</td>
<td>(\frac{\rho}{1000(MW)})</td>
<td>(\frac{\rho}{1000(MW)(T)})</td>
<td>(\frac{(\rho)(MWₐ)}{MW})</td>
<td>(\frac{(\rho)(MWₐ)}{MW}) (\times 10^{-6}) (\frac{(\rho)(MWₐ)}{MW})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Percentage (mass basis)</td>
<td>(10^4\rho)</td>
<td>(10^4\rho)</td>
<td>(10^4\rho)</td>
<td>(10^4\rho) (\frac{(10^4\rho)(MWₐ)}{MW})</td>
<td>(10^4\rho) (\frac{(10^4\rho)(MWₐ)}{MW})</td>
<td></td>
</tr>
</tbody>
</table>

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

The concentration unit ppmₐ is defined for a gas as:

\[
\frac{10^4 \left( \frac{\text{moles of species}}{\text{volume}} \right)}{\text{moles of air} \ \text{volume}}
\]
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:

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

Substituting:

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

### 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 m². Is the number concentration (also called the bather load, which equals 20 per 15 m² = 1.3 \times 10^{-3}/L) the best measure of the liveliness of the children?

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**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 MgSO₄) 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 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 solutions 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 systems 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 Hg²⁺ in water. The four species are CH₃Hg⁺, Hg²⁺, CH₄(aq), and CH₄(g). Based on the lessons of this chapter, it should be possible to select units for the four species in the chemical system.