

### 2.1.2 MASS/VOLUME UNITS: mg/L AND $\mu\text{g}/\text{m}^3$

In the atmosphere, it is common to use concentration units of mass per volume of air, such as  $\text{mg}/\text{m}^3$  and  $\mu\text{g}/\text{m}^3$ . In water, mass/volume concentration units of  $\text{mg}/\text{L}$  and  $\mu\text{g}/\text{L}$  are common. In most aqueous systems,  $\text{ppm}_m$  is equivalent to  $\text{mg}/\text{L}$ . This is because the density of pure water is approximately  $1,000 \text{ g}/\text{L}$  (demonstrated in Example 2.2).

The density of pure water is actually  $1,000 \text{ g}/\text{L}$  at  $5^\circ\text{C}$ . At  $20^\circ\text{C}$ , the density has decreased slightly to  $998.2 \text{ g}/\text{L}$ . This equality is strictly true only for *dilute* solutions, in which any dissolved material does not contribute significantly to the mass of the water, and the total density remains approximately  $1,000 \text{ g}/\text{L}$ . Most wastewaters, reclaimed waters, and natural waters can be considered dilute, except perhaps seawaters, brines, and some recycled streams.

#### example/2.2 Concentration in Water

One liter of water is analyzed and found to contain  $5.0 \text{ mg}$  of TCE. What is the TCE concentration in  $\text{mg}/\text{L}$  and  $\text{ppm}_m$ ?

#### solution

$$[\text{TCE}] = \frac{5.0 \text{ mg TCE}}{1.0 \text{ L H}_2\text{O}} = \frac{5.0 \text{ mg}}{\text{L}}$$

To convert to  $\text{ppm}_m$ , a mass/mass unit, it is necessary to convert the volume of water to mass of water. To do this, divide by the density of water, which is approximately  $1,000 \text{ g}/\text{L}$ :

$$\begin{aligned} \text{TCE} &= \frac{5.0 \text{ mg TCE}}{1.0 \text{ L H}_2\text{O}} \times \frac{1.0 \text{ L H}_2\text{O}}{1,000 \text{ g H}_2\text{O}} \\ &= \frac{5.0 \text{ mg TCE}}{1,000 \text{ g total}} = \frac{5.0 \times 10^{-6} \text{ g TCE}}{\text{g total}} \times \frac{10^6 \text{ ppm}_m}{\text{mass fraction}} \\ &= 5.0 \text{ ppm}_m \end{aligned}$$

In most dilute aqueous systems,  $\text{mg}/\text{L}$  is equivalent to  $\text{ppm}_m$ .

In this example, the TCE concentration is well above the allowable U.S. drinking water standard for TCE,  $5 \mu\text{g}/\text{L}$  (or  $5 \text{ ppb}$ ), which was set to protect human health. Five  $\text{ppb}$  is a small value. Think of it this way: Earth's population exceeds 6 billion people, meaning that 30 individuals in one of your classes constitute a human concentration of approximately  $5 \text{ ppb}$ !

## 2.2 Volume/Volume and Mole/Mole Units

Units of volume fraction or mole fraction are frequently used for gas concentrations. The most common volume fraction units are **parts per million by volume** (referred to as  $\text{ppm}_v$  or  $\text{ppm}_v$ ), defined as:

$$\text{ppm}_v = \frac{V_i}{V_{\text{total}}} \times 10^6 \quad (2.5)$$

### example/2.3 Concentration in Air

What is the carbon monoxide (CO) concentration expressed in  $\mu\text{g}/\text{m}^3$  of a  $10 \text{ L}$  gas mixture that contains  $10^{-6}$  mole of CO?

#### solution

In this case, the measured quantities are presented in units of moles of the chemical per total volume. To convert to mass of the chemical per total volume, convert the moles of chemical to mass of chemical by multiplying moles by CO's molecular weight. The molecular weight of CO ( $28 \text{ g}/\text{mole}$ ) is equal to 12 (atomic weight of C) plus 16 (atomic weight of O).

$$\begin{aligned} [\text{CO}] &= \frac{1.0 \times 10^{-6} \text{ mole CO}}{10 \text{ L total}} \times \frac{28 \text{ g CO}}{\text{mole CO}} \\ &= \frac{28 \times 10^{-6} \text{ g CO}}{10 \text{ L total}} \times \frac{10^6 \mu\text{g}}{\text{g}} \times \frac{10^3 \text{ L}}{\text{m}^3} = \frac{2,800 \mu\text{g}}{\text{m}^3} \end{aligned}$$

where  $V_i/V_{\text{total}}$  is the volume fraction and  $10^6$  is a conversion factor, with units of  $10^6 \text{ ppm}_v$  per volume fraction.

Other common units for gaseous pollutants are **parts per billion** ( $10^9$ ) by volume ( $\text{ppb}_v$ ). Table 2.2 provides examples of the change in the atmospheric concentration of three major **greenhouse gases (GHGs)** since preindustrial times, around the year 1750.

The advantage of volume/volume units is that gaseous concentrations reported in these units do not change as a gas is compressed or expanded. Atmospheric concentrations expressed as mass per volume (e.g.,  $\mu\text{g}/\text{m}^3$ ) decrease as the gas expands, since the pollutant mass remains constant but the volume increases. Both mass/volume units, such as  $\mu\text{g}/\text{m}^3$ , and  $\text{ppm}_v$  units are frequently used to express gaseous concentrations. (See Equation 2.9 for conversion between  $\mu\text{g}/\text{m}^3$  and  $\text{ppm}_v$ .)

Table / 2.2

Change in Atmospheric Concentration of Major GHGs Since Preindustrial Times

	2011 Atmospheric Concentration	Preindustrial Atmospheric Concentration	Percent Change Since Preindustrial Times
Carbon dioxide ( $\text{CO}_2$ )	391 ppm	280 ppm	+140%
Methane ( $\text{CH}_4$ )	1,813 ppb	700 ppb	+259%
Nitrous oxide ( $\text{N}_2\text{O}$ )	324 ppb	270 ppb	+120%

SOURCE: Data from World Meteorological Organization (2012).

### 2.2.1 USING THE IDEAL GAS LAW TO CONVERT ppm<sub>v</sub> TO μg/m<sup>3</sup>

The ideal gas law can be used to convert gaseous concentrations between mass/volume and volume/volume units. The **ideal gas law** states that *pressure (P)* times *volume occupied (V)* equals *the number of moles (n)* times the *gas constant (R)* times the *absolute temperature (T)* in degrees Kelvin or Rankine. This is written in the familiar form of

$$PV = nRT \quad (2.6)$$

In Equation 2.6, the **universal gas constant, R**, may be expressed in many different sets of units. Some of the most common values for R are:

$$0.08205 \text{ L-atm/mole-K}$$

$$8.205 \times 10^{-5} \text{ m}^3\text{-atm/mole-K}$$

$$82.05 \text{ cm}^3\text{-atm/mole-K}$$

$$1.99 \times 10^{-3} \text{ kcal/mole-K}$$

$$8.314 \text{ J/mole-K}$$

$$1.987 \text{ cal/mole-K}$$

$$62,358 \text{ cm}^3\text{-torr/mole-K}$$

$$62,358 \text{ cm}^3\text{-mm Hg/mole-K}$$

Because the gas constant may be expressed in different units, always be careful of its units and cancel them out to ensure you are using the correct value of R.

The ideal gas law also states that the volume occupied by a given number of molecules of any gas is the same, no matter what the molecular weight or composition of the gas, as long as the pressure and temperature are constant. The ideal gas law can be rearranged to show the volume occupied by *n* moles of gas:

$$V = n \frac{RT}{P} \quad (2.7)$$

At standard conditions ( $P = 1 \text{ atm}$  and  $T = 273.15 \text{ K}$ ), 1 mole of any pure gas will occupy a volume of 22.4 L. This result can be derived by using the corresponding value of R (0.08205 L-atm/mole-K) and the form of the ideal gas law provided in Equation 2.7. At other temperatures and pressures, this volume varies as determined by Equation 2.7.

In Example 2.4, the terms  $RT/P$  cancel out. This demonstrates an important point that is useful in calculating volume fraction or mole fraction concentrations: *For gases, volume ratios and mole ratios are equivalent.* This is clear from the ideal gas law, because at constant temperature

### example/2.4 Gas Concentration in Volume Fraction

A gas mixture contains 0.001 mole of sulfur dioxide (SO<sub>2</sub>) and 0.999 mole of air. What is the SO<sub>2</sub> concentration, expressed in units of ppm<sub>v</sub>?

#### solution

The concentration in ppm<sub>v</sub> is determined using Equation 2.5.

$$[\text{SO}_2] = \frac{V_{\text{SO}_2}}{V_{\text{total}}} \times 10^6$$

To solve, convert the number of moles of SO<sub>2</sub> to volume using the ideal gas law (Equation 2.6) and the total number of moles to volume. Then divide the two expressions:

$$V_{\text{SO}_2} = 0.001 \text{ mole SO}_2 \times \frac{RT}{P}$$

$$V_{\text{total}} = (0.999 + 0.001) \text{ mole total} \times \frac{RT}{P} \\ = (1.000) \text{ mole total} \times \frac{RT}{P}$$

Substitute these volume terms for ppm<sub>v</sub>:

$$\text{ppm}_v = \frac{0.001 \text{ mole SO}_2 \times \frac{RT}{P}}{1.000 \text{ mole total} \times \frac{RT}{P}} \times 10^6 \\ \text{ppm}_v = \frac{0.001 \text{ L SO}_2}{1.000 \text{ L total}} \times 10^6 = 1,000 \text{ ppm}_v$$

Note also that the **mole ratio** (moles *i* / moles total) is sometimes referred to as the **mole fraction, X**.

and pressure, the volume occupied by a gas is proportional to the number of moles. Therefore, Equation 2.5 is equivalent to Equation 2.8:

$$\text{ppm}_v = \frac{\text{moles } i}{\text{moles total}} \times 10^6 \quad (2.8)$$

The solution to Example 2.4 could have been found simply by using Equation 2.8 and determining the mole ratio. Therefore, in any given problem, you can use either units of volume or units of moles to calculate ppm<sub>v</sub>. Being aware of this will save unnecessary conversions between moles and volume.

Example 2.5 and Equation 2.9 show how to use the ideal gas law to convert concentrations between μg/m<sup>3</sup> and ppm<sub>v</sub>. Example 2.5 demonstrates a useful way to write the conversion for air concentrations

**example/ 2.5** Conversion of Gas Concentration between  $\text{ppb}_v$  and  $\mu\text{g}/\text{m}^3$   
 The concentration of  $\text{SO}_2$  is measured in air to be  $100 \text{ ppb}_v$ . What is this concentration in units of  $\mu\text{g}/\text{m}^3$ ? Assume the temperature is  $28^\circ\text{C}$  and pressure is  $1 \text{ atm}$ . Remember that  $T$  expressed in  $\text{K}$  is equal to  $T$  expressed in  $^\circ\text{C}$  plus  $273.15$ .

**solution**

To accomplish this conversion, use the ideal gas law to convert the volume of  $\text{SO}_2$  to moles of  $\text{SO}_2$ , resulting in units of moles/L. This can be converted to  $\mu\text{g}/\text{m}^3$  using the molecular weight of  $\text{SO}_2$  (which equals  $64$ ). This method will be used to develop a general formula for converting between  $\text{ppm}_v$  and  $\mu\text{g}/\text{m}^3$ .

First, use the definition of  $\text{ppb}_v$  to obtain a volume ratio for  $\text{SO}_2$ :

$$100 \text{ ppb}_v = \frac{100 \text{ m}^3 \text{ SO}_2}{10^9 \text{ m}^3 \text{ air solution}}$$

Now convert the volume of  $\text{SO}_2$  in the numerator to units of mass. This is done in two steps. First, convert the volume to a number of moles, using a rearranged format of the ideal gas law (Equation 2.6),  $n/V = P/RT$ , and the given temperature and pressure:

$$\frac{100 \text{ m}^3 \text{ SO}_2}{10^9 \text{ m}^3 \text{ air solution}} \times \frac{P}{RT} = \frac{100 \text{ m}^3 \text{ SO}_2}{10^9 \text{ m}^3 \text{ air solution}} \times \frac{1 \text{ atm}}{8.205 \times 10^{-5} \frac{\text{m}^3 \cdot \text{atm}}{\text{mole} \cdot \text{K}} (301\text{K})} = \frac{4.05 \times 10^{-6} \text{ mole SO}_2}{\text{m}^3 \text{ air}}$$

In the second step, convert the moles of  $\text{SO}_2$  to mass of  $\text{SO}_2$  by using the molecular weight of  $\text{SO}_2$ :

$$\frac{4.05 \times 10^{-6} \text{ mole SO}_2}{\text{m}^3 \text{ air}} \times \frac{64 \text{ g SO}_2}{\text{mole SO}_2} \times \frac{10^6 \mu\text{g}}{\text{g}} = \frac{260 \mu\text{g}}{\text{m}^3}$$

between units of  $\mu\text{g}/\text{m}^3$  and  $\text{ppm}_v$ :

$$\frac{\mu\text{g}}{\text{m}^3} = \text{ppm}_v \times \text{MW} \times \frac{1,000P}{RT} \quad (2.9)$$

where  $\text{MW}$  is the molecular weight of the chemical species,  $R$  equals  $0.08205 \text{ L} \cdot \text{atm}/\text{mole} \cdot \text{K}$ ,  $T$  is the temperature in  $\text{K}$ , and  $1,000$  is a conversion factor ( $1,000 \text{ L} = \text{m}^3$ ). Note that for  $0^\circ\text{C}$ ,  $RT$  has a value of  $22.4 \text{ L} \cdot \text{atm}/\text{mole}$ , while at  $20^\circ\text{C}$ ,  $RT$  has a value of  $24.1 \text{ L} \cdot \text{atm}/\text{mole}$ .

**2.3 Partial-Pressure Units**

In the atmosphere, concentrations of chemicals in the gas and particulate phases may be determined separately. A substance will exist in the gas phase if the atmospheric temperature is above the substance's boiling (or sublimation) point or if its concentration is below the saturated vapor pressure of the chemical at a specified

**Nitrogen Dioxide Air Pollution**

[www.epa.gov/air/nitrogenoxides](http://www.epa.gov/air/nitrogenoxides)

**Atmospheric  $\text{NO}_2$  Air Quality Over Time**

[www.epa.gov/airtrends/nitrogen.html](http://www.epa.gov/airtrends/nitrogen.html)

**Table / 2.3**

**Composition of the Atmosphere**

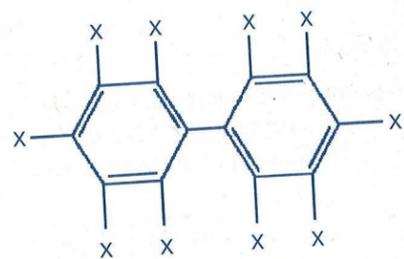
Compound	Concentration (% volume or moles)	Concentration ( $\text{ppm}_v$ )
Nitrogen ( $\text{N}_2$ )	78.1	781,000
Oxygen ( $\text{O}_2$ )	20.9	209,000
Argon (Ar)	0.93	9,300
Carbon dioxide ( $\text{CO}_2$ )	0.039	391
Neon (Ne)	0.0018	18
Helium (He)	0.0005	5
Methane ( $\text{CH}_4$ )	0.00018	1.813
Krypton (Kr)	0.00011	1.1
Hydrogen ( $\text{H}_2$ )	0.00005	0.50
Nitrous oxide ( $\text{N}_2\text{O}$ )	0.000032	0.324
Ozone ( $\text{O}_3$ )	0.000002	0.020

SOURCE: 2011 Values updated from Mihelcic (1999); with permission of John Wiley & Sons, Inc.

temperature (vapor pressure is defined in Chapter 3). The major and minor gaseous constituents of the atmosphere all have boiling points well below atmospheric temperatures. Concentrations of these species typically are expressed as either volume fractions (for example, percent,  $\text{ppm}_v$ , or  $\text{ppb}_v$ ) or partial pressures (units of atmospheres).

Table 2.3 summarizes the concentrations of the most abundant atmospheric gaseous constituents, including carbon dioxide and methane. Carbon dioxide is the largest human contributor to GHGs in the atmosphere. The global atmospheric concentration of carbon dioxide has increased to  $391 \text{ ppm}_v$  in 2011 from preindustrial revolution levels of  $280 \text{ ppm}_v$ . Global atmospheric concentrations of methane recorded in 2011 have reached  $1,813 \text{ ppb}$ . This recorded methane concentration greatly exceeds the natural range of  $320\text{--}790 \text{ ppb}_v$ , measured in ice cores, that dates over the past  $650,000$  years. According to the **Intergovernmental Panel on Climate Change** (IPCC, see [www.ipcc.ch](http://www.ipcc.ch)), it is very likely that this increase in methane concentration is due to agricultural land use, population growth, and energy use associated with burning fossil fuels.

The total pressure exerted by a gas mixture may be considered as the sum of the partial pressures exerted by each component of the mixture. The **partial pressure** of each component is equal to the pressure that would be exerted if all of the other components of the mixture were suddenly removed. Partial pressure is commonly written as  $P_i$ , where  $i$  refers to a particular gas. For example, the partial pressure of oxygen in the atmosphere  $P_{\text{O}_2}$  is  $0.21 \text{ atm}$ .



X = chlorine or hydrogen

**Figure / 2.1** Chemical Structure of Polychlorinated Biphenyls (PCBs)

PCBs are a family of compounds produced commercially by chlorinating biphenyl. Chlorine atoms can be placed at any or all of 10 available sites, with 209 possible PCB congeners. The great stability of PCBs caused them to have a wide range of uses, including serving as coolants in transformers and as hydraulic fluids and solvents. However, the chemical properties that resulted in this stability also resulted in a chemical that did not degrade easily, bioaccumulated in the food chain, and was hazardous to humans and wildlife. The 1976 Toxic Substances Control Act (TSCA) banned the manufacture of PCBs and PCB-containing products. TSCA also established strict regulations regarding the future use and sale of PCBs. PCBs typically were sold as mixtures commonly referred to as Arochlors. For example, the Arochlor 1260 mixture consists of 60 percent chlorine by weight, meaning the individual PCBs in the mixture primarily are substituted with 6–9 chlorines per biphenyl molecule. In contrast, Arochlor 1242 consists of 42 percent chlorine by weight; thus, it primarily consists of PCBs with 1–6 substituted chlorines per biphenyl molecule.

[From Mihelcic (1999). Reprinted with permission of John Wiley & Sons, Inc.]

Remember, the ideal gas law states that, at a given temperature and volume, pressure is directly proportional to the number of moles of gas present; therefore, pressure fractions are identical to mole fractions (and volume fractions). For this reason, partial pressure can be calculated as the product of the mole or volume fraction and the total pressure. For example:

$$P_i = [\text{volume fraction}_i \text{ or mole fraction}_i \times P_{\text{total}}] \quad (2.10)$$

$$= [(\text{ppm}_v)_i \times 10^{-6} \times P_{\text{total}}]$$

Rearranging Equation 2.10 shows that  $\text{ppm}_v$  values can be calculated from partial pressures as follows:

$$\text{ppm}_v = \frac{P_i}{P_{\text{total}}} \times 10^6 \quad (2.11)$$

Partial pressure can thus be added to the list of unit types that can be used to calculate  $\text{ppm}_v$ . That is, either volume (Equation 2.5), moles (Equation 2.8), or partial pressures (Equation 2.11) can be used in  $\text{ppm}_v$  calculations.

Example 2.6 applies these principles to the partial pressure of a formerly popular family of chemical compounds known as PCBs, as illustrated in Figure 2.1.

## 2.4 Mole/Volume Units

Units of **moles per liter** (molarity, M) are used to report concentrations of compounds dissolved in water. **Molarity** is defined as the number of moles of compound per liter of solution. Concentrations expressed in these units are read as **molar**.

Molarity, M, should not be confused with molality, m. Molarity is usually used in equilibrium calculations and throughout the remainder of this book. **Molality** is the number of moles of a solute added to exactly 1 L of solvent. Thus, the actual volume of a molal solution is slightly larger than 1 L. Molality is more likely to be used when properties of the solvent, such as boiling and freezing points, are a concern. Therefore, it is rarely used in environmental situations.

### example / 2.6 Concentration as Partial Pressure

The concentration of gas-phase PCBs in the air above Lake Superior was measured to be 450 picograms per cubic meter ( $\text{pg}/\text{m}^3$ ). What is the partial pressure (in atm) of PCBs? Assume the temperature is  $0^\circ\text{C}$ , the atmospheric pressure is 1 atm, and the average molecular weight of PCBs is 325.

#### solution

The partial pressure is defined as the mole or volume fraction times the total gas pressure. First, find the number of moles of PCBs in a liter of air. Then use the ideal gas law (Equation 2.7) to calculate that 1 mole of gas at  $0^\circ\text{C}$  and 1 atm occupies 22.4 L. Substitute this value into the first expression to determine the mole fraction of PCBs:

$$450 \frac{\text{pg}}{\text{m}^3 \text{ air}} \times \frac{\text{mole}}{325 \text{ g}} \times 10^{-12} \frac{\text{g}}{\text{pg}} \times 10^{-3} \frac{\text{m}^3}{\text{L}} = 1.38 \times 10^{-15} \frac{\text{mole PCB}}{\text{L air}}$$

$$1.38 \times 10^{-15} \frac{\text{mole PCB}}{\text{L air}} \times \frac{22.4 \text{ L}}{\text{mole air}} = 3.1 \times 10^{-14} \frac{\text{mole PCB}}{\text{mole air}}$$

Multiplying the mole fraction by the total pressure (1 atm) (see Equation 2.10) yields the PCB partial pressure of  $3.1 \times 10^{-14}$  atm.

### example / 2.7 Concentration as Partial Pressure Corrected for Moisture

What would be the partial pressure (in atm) of carbon dioxide ( $\text{CO}_2$ ) when the barometer reads 29.0 inches of Hg, the relative humidity is 80 percent, and the temperature is  $70^\circ\text{F}$ ? Use Table 2.3 to obtain the concentration of  $\text{CO}_2$  in dry air.

#### solution

The partial-pressure concentration units in Table 2.3 are for dry air, so the partial pressure must first be corrected for the moisture present in the air. In dry air, the  $\text{CO}_2$  concentration is 391  $\text{ppm}_v$ . The partial pressure will be this volume fraction times the total pressure of dry air. The total pressure of dry air is the total atmospheric pressure (29.0 in. Hg) minus the contribution of water vapor. The vapor pressure of water at  $70^\circ\text{F}$  is  $0.36 \text{ lb}/\text{in}^2$ . Thus, the total pressure of dry air is

$$P_{\text{total}} - P_{\text{water}} = 29.0 \text{ in. Hg} - \left[ 0.36 \frac{\text{lb}}{\text{in}^2} \times \frac{29.9 \text{ in. Hg}}{14.7 \text{ lb}/\text{in}^2} \times 0.8 \right]$$

$$= 28.4 \text{ in. Hg}$$

The partial pressure of  $\text{CO}_2$  would be:

$$\text{vol. fraction} \times P_{\text{total}} = 391 \text{ ppm}_v \times \frac{10^{-6} \text{ vol. fraction}}{\text{ppm}_v} \times \left[ 28.4 \text{ in. Hg} \times \frac{1 \text{ atm}}{29.9 \text{ in. Hg}} \right] = 3.7 \times 10^{-4} \text{ atm}$$

### example/2.8 Concentration as Molarity

The concentration of TCE is 5 ppm. Convert this to units of molarity. The molecular weight of TCE is 131.5 g/mole.

#### solution

Remember, in water, ppm<sub>m</sub> is equivalent to mg/L, so the concentration of TCE is 5.0 mg/L. Conversion to molarity units requires only the molecular weight:

$$\frac{5.0 \text{ mg TCE}}{\text{L}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} \times \frac{1 \text{ mole}}{131.5 \text{ g}} = \frac{3.8 \times 10^{-5} \text{ moles}}{\text{L}} \\ = 3.8 \times 10^{-5} \text{ M}$$

Often, concentrations below 1 M are expressed in units of millimoles per liter, or millimolar (1 mM = 10<sup>-3</sup> moles/L), or in micromoles per liter, or micromolar (1 μM = 10<sup>-6</sup> moles/L). Thus, the concentration of TCE could be expressed as 0.038 mM or 38 μM.

### example/2.9 Concentration as Molarity

The concentration of alachlor, a common herbicide, in the Mississippi River was found to range from 0.04 to 0.1 μg/L. What is the concentration range in nmoles/L? The molecular formula for alachlor is C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>NCl, and its molecular weight is 270.

#### solution

The lowest concentration range in nmoles/L can be found as follows:

$$\frac{0.04 \text{ } \mu\text{g}}{\text{L}} \times \frac{\text{mole}}{270 \text{ g}} \times \frac{10^{-6} \text{ g}}{\mu\text{g}} \times \frac{10^9 \text{ nmole}}{\text{mole}} = \frac{0.15 \text{ nmole}}{\text{L}}$$

Similarly, the upper limit (0.1 μg/L) can be calculated as 0.37 nmoles/L.

## 2.5 Other Types of Units

Concentrations can also be expressed as normality, expressed as a common constituent, or represented by effect.

### 2.5.1 NORMALITY

**Normality** (equivalents/L) typically is used in defining the chemistry of water, especially in instances where acid–base and oxidation–reduction reactions are taking place. Normality is also used frequently in the laboratory during the analytical measurement of water constituents. For example, “Standard Methods for the Examination of Water and Wastewater” has many examples where concentrations of chemical reagents are prepared and reported in units of normality and not molarity.

Reporting concentration on an **equivalent basis** is useful because if two chemical species react and the two species reacting have the same strength on an equivalent basis, a 1 mL volume of reactant number 1 will react with a 1 mL volume of reactant number 2. In acid–base chemistry, the number



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### example/2.10 Calculations of Equivalent Weight

What are the equivalent weights of HCl, H<sub>2</sub>SO<sub>4</sub>, NaOH, CaCO<sub>3</sub>, and aqueous CO<sub>2</sub>?

#### solution

To find the equivalent weight of each compound, divide the molecular weight by the number of equivalents:

$$\text{eqv wt of HCl} = \frac{(1 + 35.5)\text{g/mole}}{1 \text{ eqv/mole}} = \frac{36.5 \text{ g}}{\text{eqv}}$$

$$\text{eqv wt of H}_2\text{SO}_4 = \frac{(2 \times 1) + 32 + (4 \times 16)\text{g/mole}}{2 \text{ eqv/mole}} = \frac{49 \text{ g}}{\text{eqv}}$$

$$\text{eqv wt of NaOH} = \frac{(23 + 16 + 1)\text{g/mole}}{1 \text{ eqv/mole}} = \frac{40 \text{ g}}{\text{eqv}}$$

$$\text{eqv wt of CaCO}_3 = \frac{40 + 12 + (3 \times 16)\text{g/mole}}{2 \text{ eqv/mole}} = \frac{50 \text{ g}}{\text{eqv}}$$

Determining the equivalent weight of aqueous CO<sub>2</sub> requires additional information. Aqueous carbon dioxide is not an acid until it hydrates in water and forms carbonic acid (CO<sub>2</sub> + H<sub>2</sub>O → H<sub>2</sub>CO<sub>3</sub>). So aqueous CO<sub>2</sub> really has 2 eqv/mole. Thus, one can see that the equivalent weight of aqueous carbon dioxide is

$$\frac{12 + (2 \times 16)\text{g/mole}}{2 \text{ eqv/mole}} = \frac{22 \text{ g}}{\text{eqv}}$$

of equivalents per mole of acid equals the number of moles of H<sup>+</sup> the acid can potentially donate. For example, HCl has 1 equivalent/mole, H<sub>2</sub>SO<sub>4</sub> has 2 equivalents/mole, and H<sub>3</sub>PO<sub>4</sub> has 3 equivalents/mole. Likewise, the number of equivalents per mole of a base equals the number of moles of H<sup>+</sup> that will react with 1 mole of the base. Thus, NaOH has 1 equivalent/mole, CaCO<sub>3</sub> has 2 equivalents/mole, and PO<sub>4</sub><sup>3-</sup> has 3 equivalents/mole.

In oxidation–reduction reactions, the number of equivalents is related to how many electrons a species donates or accepts. For example, the number of equivalents of Na<sup>+</sup> is 1 (where e<sup>-</sup> equals an electron) because Na → Na<sup>+</sup> + e<sup>-</sup>. Likewise, the number of equivalents for Ca<sup>2+</sup> is 2 because Ca → Ca<sup>2+</sup> + 2e<sup>-</sup>. The **equivalent weight** (in grams (g) per equivalent (eqv)) of a species is defined as the molecular weight of the species divided by the number of equivalents in the species (g/mole divided by eqv/mole equals g/eqv).

All aqueous solutions must maintain charge neutrality. Another way to state this is that the sum of all cations on an equivalent basis must equal the sum of all anions on an equivalent basis. Thus, water samples can be checked to determine whether something is incorrect in the analyses or a constituent is missing. Example 2.12 showed how this is done.

### example/2.11 Calculation of Normality

What is the normality (N) of 1 M solutions of HCl and H<sub>2</sub>SO<sub>4</sub>?

#### solution

$$1 \text{ M HCl} = \frac{1 \text{ mole HCl}}{\text{L}} \times \frac{1 \text{ eqv}}{\text{mole}} = \frac{1 \text{ eqv}}{\text{L}} = 1 \text{ N}$$

$$1 \text{ M H}_2\text{SO}_4 = \frac{1 \text{ mole H}_2\text{SO}_4}{\text{L}} \times \frac{2 \text{ eqv}}{\text{mole}} = \frac{2 \text{ eqv}}{\text{L}} = 2 \text{ N}$$

Note that on an equivalent basis, a 1 M solution of sulfuric acid is twice as strong as a 1 M solution of HCl.

### example/2.12 Use of Equivalents in Determining the Accuracy of a Water Analysis

Prof. Mihelcic was in the city of Dunedin in New Zealand to view yellow-eyed penguins and albatrosses. The label on a bottle of New Zealand mineral water he purchased there states that a chemical analysis of the mineral water resulted in the following cations and anions being identified with corresponding concentrations (in mg/L):

$$[\text{Ca}^{2+}] = 2.9 \quad [\text{Mg}^{2+}] = 2.0 \quad [\text{Na}^+] = 11.5 \quad [\text{K}^+] = 3.3$$

$$[\text{SO}_4^{2-}] = 4.7 \quad [\text{F}^-] = 0.09 \quad [\text{Cl}^-] = 7.7$$

Is the analysis correct?

#### solution

First, convert all concentrations of major ions to an equivalent basis. To do this, multiply the concentration in mg/L by a unit conversion (g/1,000 mg) and then divide by the equivalent weight of each substance (g/eqv). Then sum the concentrations of all cations and anions on an equivalent basis. A solution with less than 5 percent error generally is considered acceptable.

#### Cations

$$[\text{Ca}^{2+}] = \frac{1.45 \times 10^{-4} \text{ eqv}}{\text{L}}$$

$$[\text{Mg}^{2+}] = \frac{1.67 \times 10^{-4} \text{ eqv}}{\text{L}}$$

$$[\text{Na}^+] = \frac{5 \times 10^{-4} \text{ eqv}}{\text{L}}$$

$$[\text{K}^+] = \frac{8.5 \times 10^{-5} \text{ eqv}}{\text{L}}$$

#### Anions

$$[\text{SO}_4^{2-}] = \frac{9.75 \times 10^{-5} \text{ eqv}}{\text{L}}$$

$$[\text{F}^-] = \frac{4.73 \times 10^{-6} \text{ eqv}}{\text{L}}$$

$$[\text{Cl}^-] = \frac{2.17 \times 10^{-4} \text{ eqv}}{\text{L}}$$

The total amount of cations equals  $9.87 \times 10^{-4}$  eqv/L, and the total amount of anions equals  $3.2 \times 10^{-4}$  eqv/L.

The analysis is not within 5 percent. The analysis resulted in more than three times more cations than anions on an equivalent basis. Therefore, either of two conclusions is possible: (1) One or more of the reported concentrations are incorrect, assuming all major cations and anions are accounted for. (2) One or more important anions were not accounted for by the chemical analysis. (Bicarbonate, HCO<sub>3</sub><sup>-</sup>, would be a good guess for the missing anion, as it is a common anion in most natural waters.)

### 2.5.2 CONCENTRATION AS A COMMON CONSTITUENT

Concentrations can be reported as a **common constituent** and can therefore include contributions from a number of different chemical compounds. GHGs, nitrogen, and phosphorus are chemicals that have their concentration typically reported as a common constituent.

For example, the phosphorus in a lake, estuary, untreated, or reclaimed wastewater may be present in inorganic forms called orthophosphates (H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, HPO<sub>4</sub><sup>2-</sup> complexes), polyphosphates (e.g., H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and H<sub>3</sub>P<sub>3</sub>O<sub>10</sub><sup>2-</sup>), metaphosphates (e.g., HP<sub>3</sub>O<sub>9</sub><sup>2-</sup>), and/or organic phosphates. Because phosphorus can be chemically converted between these forms and can thus be found in several of these forms, it makes sense at some times to report the total P concentration, without specifying which form(s) are present. Thus, each concentration for every individual form of phosphorus is converted to mg P/L using the molecular weight of the individual species, the molecular weight of P (which is 32), and simple stoichiometry. These converted concentrations of each individual species can then be added to determine the total phosphorus concentration. The concentration is then reported in units of mg/L as phosphorus (written as mg P/L, mg/L as P, or mg/L P).

The alkalinity and hardness of a water typically are reported by determining all of the individual species that contribute to either alkalinity or hardness, then converting each of these species to **units of mg CaCO<sub>3</sub>/L**, and finally summing up the contribution of each species. Hardness is thus typically expressed as mg/L as CaCO<sub>3</sub>.

The **hardness** of a water is caused by the presence of divalent cations in water. Ca<sup>2+</sup> and Mg<sup>2+</sup> are by far the most abundant divalent cations in natural waters, though Fe<sup>2+</sup>, Mn<sup>2+</sup>, and Sr<sup>2+</sup> may contribute as well.

### example/2.13 Nitrogen Concentrations as a Common Constituent

A water contains two nitrogen species. The concentration of NH<sub>3</sub> is 30 mg/L NH<sub>3</sub>, and the concentration of NO<sub>3</sub><sup>-</sup> is 5 mg/L NO<sub>3</sub><sup>-</sup>. What is the total nitrogen concentration in units of mg N/L?

#### solution

Use the appropriate molecular weight and stoichiometry to convert each individual species to the requested units of mg N/L and then add the contribution of each species:

$$\frac{30 \text{ mg NH}_3}{\text{L}} \times \frac{\text{mole NH}_3}{17 \text{ g}} \times \frac{\text{mole N}}{\text{mole NH}_3} \times \frac{14 \text{ g}}{\text{mole N}} = \frac{24.7 \text{ mg NH}_3 - \text{N}}{\text{L}}$$

$$\frac{5 \text{ mg NO}_3^-}{\text{L}} \times \frac{\text{mole NO}_3^-}{62 \text{ g}} \times \frac{\text{mole N}}{\text{mole NO}_3^-} \times \frac{14 \text{ g}}{\text{mole N}} = \frac{1.1 \text{ mg NO}_3^- - \text{N}}{\text{L}}$$

$$\text{total nitrogen concentration} = 24.7 + 1.1 = \frac{25.8 \text{ mg N}}{\text{L}}$$

#### Nitrogen and Phosphorus Pollution Policy and Data

[www.epa.gov/nandppolicy/index.html](http://www.epa.gov/nandppolicy/index.html)

#### Nutrient-Caused Hypoxia in the Gulf of Mexico

[toxics.usgs.gov/hypoxia](http://toxics.usgs.gov/hypoxia)

#### The Nitrogen Cycle

[www.esrl.noaa.gov/gmd/outreach/lesson\\_plans/The Nitrogen Cycle.pdf](http://www.esrl.noaa.gov/gmd/outreach/lesson_plans/The%20Nitrogen%20Cycle.pdf)

In Michigan, Wisconsin, and Minnesota, untreated waters usually have a hardness of 121–180 mg/L as CaCO<sub>3</sub>. In Illinois, Iowa, and Florida water is harder, with many values greater than 180 mg/L as CaCO<sub>3</sub>.

To find the total hardness of a water sample, sum the contributions of all divalent cations after converting their concentrations to a common constituent. To convert the concentration of specific cations (from mg/L) to hardness (as mg/L CaCO<sub>3</sub>), use the following expression, where M<sup>2+</sup> represents a divalent cation:

$$\frac{M^{2+} \text{ in mg}}{L} \times \frac{50}{\text{eqv wt of } M^{2+} \text{ in g/eqv}} = \frac{\text{mg}}{L} \text{ as CaCO}_3 \quad (2.13)$$

The 50 in Equation 2.13 represents the equivalent weight of calcium carbonate (100 g CaCO<sub>3</sub>/2 equivalents). The equivalent weights (in units of g/eqv) of other divalent cations are Mg, 24/2; Ca, 40/2; Mn, 55/2; Fe, 56/2; and Sr, 88/2.

### 2.5.3 CONCENTRATIONS OF CARBON DIOXIDE AND OTHER GHGs

The **Kyoto Protocol** is a global agreement to regulate six major GHGs. It was adopted in Kyoto, Japan, in 1997 and entered into force in 2005. It sets binding targets for 37 industrialized countries and the European Union to reduce GHG emissions. Each gas has a different ability to

absorb heat in the atmosphere (the radiative forcing), so each differs in its global warming potential (GWP). The Kyoto Protocol has been ratified by 191 states (i.e., countries). However, it was not adopted by many large emitters of GHGs, including the United States. Furthermore, in 2011, Canada renounced their earlier support.

Though the U.S. government has not ratified the Kyoto Protocol, in 2007, the U.S. Supreme Court ruled that EPA has the authority under the Clean Air Act to regulate emissions of carbon dioxide and other GHGs. In October 30, 2009, EPA published a rule in the Federal Register (40 CFR Part 98) that required mandatory reporting of GHGs from large sources. The implementation of this rule is referred to as the **Greenhouse Gas Reporting Program**. It applies to a wide range of GHG emitters that includes fossil fuel suppliers, industrial gas suppliers, and facilities that inject CO<sub>2</sub> underground for sequestration. This movement to regulate GHGs as air pollutants was further confirmed in 2012 when the U.S. Court of Appeals for the District of Columbia unanimously upheld the first ever proposed regulations to regulate emissions of GHGs.

The **global warming potential (GWP)** is a multiplier used to compare the emissions of different greenhouse gases to a common constituent, in this case carbon dioxide. The GWP is determined over a set time period, typically 100 years, over which the radiative forcing of the specific gas would result. GWPs allow policy makers to compare emissions and reductions of specific gases.

**Carbon dioxide equivalents** are a metric measure used to compare the mass emissions of greenhouse gases to a common constituent, based on the specific gas's global warming potential. Units are mass based and typically a million metric tons of carbon dioxide equivalents. Table 2.4 provides global warming potentials for the six major greenhouse gases. Note that an equivalent mass release of two greenhouse gases does not have the same impact on global warming. For example, from Table 2.4, we can see that 1 ton of methane emissions equates to 25 tons of carbon dioxide emissions.

#### example/2.14 Determination of a Water's Hardness

Water has the following chemical composition: [Ca<sup>+</sup>] = 15 mg/L; [Mg<sup>2+</sup>] = 10 mg/L; [SO<sub>4</sub><sup>2-</sup>] = 30 mg/L. What is the total hardness in units of mg/L as CaCO<sub>3</sub>?

#### solution

Find the contribution of hardness from each divalent cation. Anions and all nondivalent cations are not included in the calculation.

$$\frac{15 \text{ mg Ca}^{2+}}{L} \times \left( \frac{50 \text{ g CaCO}_3}{\text{eqv}} \div \frac{40 \text{ g Ca}^{2+}}{2 \text{ eqv}} \right) = \frac{38 \text{ mg}}{L} \text{ as CaCO}_3$$

$$\frac{10 \text{ mg Mg}^{2+}}{L} \times \left( \frac{50 \text{ g CaCO}_3}{\text{eqv}} \div \frac{24 \text{ g Mg}^{2+}}{2 \text{ eqv}} \right) = \frac{42 \text{ mg}}{L} \text{ as CaCO}_3$$

Therefore, the total hardness is 38 + 42 = 80 mg/L as CaCO<sub>3</sub>. This water is moderately hard. Note that if reduced iron (Fe<sup>2+</sup>) or manganese (Mn<sup>2+</sup>) were present, they would be included in the hardness calculation.

Table / 2.4

#### 100-Year Global Warming Potentials (GWPs) Used to Convert Mass Greenhouse Gas Emissions to Carbon Dioxide Equivalents (CO<sub>2</sub>e)

Type of Emission	Multiplier for CO <sub>2</sub> Equivalents (CO <sub>2</sub> e)
Carbon dioxide	1
Methane	25
Nitrous oxide	298
Hydrofluorocarbons (HFCs)	124–14,800 (depends on specific HFC)
Perfluorocarbons (PFCs)	7,390–12,200 (depends on specific PFC)
Sulfur hexafluoride (SF <sub>6</sub> )	22,800

SOURCE: Values from *Climate Change 2007: A Physical Science Basis*, Intergovernmental Panel on Climate Change. Note that EPA reports that they use 100-year GWPs listed in the IPCC's Second Assessment Report to be consistent with the international standards under the United Nations Framework Convention on Climate Change.

#### Greenhouse Gas Reporting Program

[www.epa.gov/ghgreporting](http://www.epa.gov/ghgreporting)

#### Regulating Greenhouse Gases

[www.epa.gov/climatechange/endorsement](http://www.epa.gov/climatechange/endorsement)

#### United Nations Framework Convention on Climate Change

<http://unfccc.int>

#### Intergovernmental Panel on Climate Change

[www.ipcc.ch](http://www.ipcc.ch)