

One calorie is the energy required to heat 1 gram of water from 14.5° to 15.5°C. One joule is the energy expended when a force of 1 newton acts over a distance of 1 meter. This much energy can raise 102 g (about $\frac{1}{4}$ pound) by 1 meter.

$$1 \text{ cal} = 4.184 \text{ J}$$

1 pound (mass) = 0.453 6 kg
1 mile = 1.609 km
The symbol \approx is read “is approximately equal to.”

Significant figures are discussed in Chapter 3. For multiplication and division, the number with the fewest digits determines how many digits should be in the answer. The number of kcal at the beginning of this problem limits the answer to 2 digits.

A homogeneous substance has a uniform composition. Sugar dissolved in water is homogeneous. A mixture that is not the same everywhere (such as orange juice, which has suspended solids) is heterogeneous.

Avogadro's number =
number of atoms in 12 g of ^{12}C

Molarity (M) = $\frac{\text{moles of solute}}{\text{liters of solution}}$

Atomic masses are shown in the periodic table inside the cover of this book. Physical constants such as Avogadro's number are also listed inside the cover.

Strong electrolyte: mostly dissociated into ions in solution
weak electrolyte: partially dissociated into ions in solution

MgO^{+} is called an ion pair. See Box 7-1.

units for energy are the calorie (cal) and the Calorie (written with a capital C and standing for 1 000 calories, or 1 kcal). Table 1-4 states that 1 cal is exactly 4.184 J (joules).

Your basal metabolism uses approximately 46 Calories per hour (h) per 100 pounds (lb) of body mass just to carry out basic functions required for life, apart from doing any kind of exercise. A person walking at 2 miles per hour on a level path uses approximately 45 Calories per hour per 100 pounds of body mass beyond basal metabolism. The same person swimming at 2 miles per hour consumes 360 Calories per hour per 100 pounds beyond basal metabolism.

EXAMPLE Unit Conversions

Express the rate of energy used by a person walking 2 miles per hour ($46 + 45 = 91$ Calories per hour per 100 pounds of body mass) in kilojoules per hour per kilogram of body mass.

Solution We will convert each non-SI unit separately. First, note that 91 Calories = 91 kcal. Table 1-4 states that 1 cal = 4.184 J; so 1 kcal = 4.184 kJ, and

$$91 \text{ kcal} \times 4.184 \frac{\text{kJ}}{\text{kcal}} = 3.8 \times 10^2 \text{ kJ}$$

Table 1-4 also says that 1 lb is 0.453 6 kg; so 100 lb = 45.36 kg. The rate of energy consumption is therefore

$$\frac{91 \text{ kcal/h}}{100 \text{ lb}} = \frac{3.8 \times 10^2 \text{ kJ/h}}{45.36 \text{ kg}} = 8.4 \frac{\text{kJ/h}}{\text{kg}}$$

We could have written this as one long calculation:

$$\text{Rate} = \frac{91 \text{ kcal/h}}{100 \text{ lb}} \times 4.184 \frac{\text{kJ}}{\text{kcal}} \times \frac{1\text{h}}{0.453 6 \text{ kg}} = 8.4 \frac{\text{kJ/h}}{\text{kg}}$$

Test Yourself A person swimming at 2 miles per hour requires 360 + 46 Calories per hour per 100 pounds of body mass. Express the energy use in kJ/h per kg of body mass. (Answer: 37 kJ/h per kg)

1-2 Chemical Concentrations

A solution is a homogeneous mixture of two or more substances. A minor species in a solution is called solute, and the major species is the solvent. In this book, most discussions concern aqueous solutions, in which the solvent is water. Concentration states how much solute is contained in a given volume or mass of solution or solvent.

Molarity and Molality

A mole (mol) is Avogadro's number of particles (atoms, molecules, ions, or anything else). Molarity (M) is the number of moles of a substance per liter of solution. A liter (L) is the volume of a cube that is 10 cm on each edge. Because $10 \text{ cm} = 0.1 \text{ m}$, $1 \text{ L} = (0.1 \text{ m})^3 = 10^{-3} \text{ m}^3$. Chemical concentrations, denoted with square brackets, are usually expressed in moles per liter (M). Thus “[H^+]” means “the concentration of H^+ .”

The atomic mass of an element is the number of grams containing Avogadro's number of atoms.¹ The molecular mass of a compound is the sum of atomic masses of the atoms in the molecule. It is the number of grams containing Avogadro's number of molecules.

An electrolyte is a substance that dissociates into ions in solution. In general, electrolytes are more dissociated in water than in other solvents. We refer to a compound that is mostly dissociated into ions as a strong electrolyte. One that is partially dissociated is called a weak electrolyte.

Magnesium chloride is a strong electrolyte. In 0.44 M MgCl_2 solution, 70% of the magnesium is free Mg^{2+} and 30% is MgCl^+ . The concentration of MgCl_2 molecules is close to 0. Sometimes the molarity of a strong electrolyte is called the formal concentration (F), to emphasize that the substance is really converted into other species in solution. When we

say that the “concentration” of MgCl_2 is 0.054 M in seawater, we are really speaking of its formal concentration (0.054 F). The “molecular mass” of a strong electrolyte is called the formula mass (FM), because it is the sum of atomic masses of atoms in the formula, even though there are very few molecules with that formula. We are going to use the abbreviation FM for both formula mass and molecular mass.

EXAMPLE Molarity of Salts in the Sea

- (a) Typical seawater contains 2.7 g of salt (sodium chloride, NaCl) per 100 mL ($= 100 \times 10^{-3} \text{ L}$). What is the molarity of NaCl in the ocean? (b) MgCl_2 has a concentration of 0.054 M in the ocean. How many grams of MgCl_2 are present in 25 mL of seawater?

Solution (a) The molecular mass of NaCl is $22.99 \text{ g/mol} (\text{Na}) + 35.45 \text{ g/mol} (\text{Cl}) = 58.44 \text{ g/mol}$. The moles of salt in 2.7 g are $(2.7 \text{ g})/(58.44 \text{ g/mol}) = 0.046 \text{ mol}$, so the molarity is

$$\text{Molarity of NaCl} = \frac{\text{mol NaCl}}{\text{L of seawater}} = \frac{0.046 \text{ mol}}{100 \times 10^{-3} \text{ L}} = 0.46 \text{ M}$$

(b) The molecular mass of MgCl_2 is $24.30 \text{ g/mol} (\text{Mg}) + 2 \times 35.45 \text{ g/mol} (\text{Cl}) = 95.20 \text{ g/mol}$. The number of grams in 25 mL is

$$\text{Grams of MgCl}_2 = \left(0.054 \frac{\text{mol}}{\text{L}}\right) \left(95.20 \frac{\text{g}}{\text{mol}}\right) (25 \times 10^{-3} \text{ L}) = 0.13 \text{ g}$$

Test Yourself Calculate the formula mass of CaSO_4 . What is the molarity of CaSO_4 in a solution containing 1.2 g of CaSO_4 in a volume of 50 mL? How many grams of CaSO_4 are in 50 mL of 0.086 M CaSO_4 ? (Answer: 136.14 g/mol, 0.18 M, 0.59 g)

For a weak electrolyte such as acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, some of the molecules dissociate into ions in solution:



Formal concentration	Percent dissociated
0.10 F	1.3%
0.010 F	4.1%
0.0010 F	12%

Molarity (m) is concentration expressed as moles of substance per kilogram of solvent (not total solution). Molarity is independent of temperature. Molarity changes with temperature because the volume of a solution usually increases when it is heated.

Percent Composition

The percentage of a component in a mixture or solution is usually expressed as a weight percent (wt%):

$$\text{Weight percent} = \frac{\text{mass of solute}}{\text{mass of total solution or mixture}} \times 100 \quad (1-1)$$

A common form of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) is 95 wt%; this expression means 95 g of ethanol per 100 g of total solution. The remainder is water. Volume percent (vol%) is defined as

$$\text{Volume percent} = \frac{\text{volume of solute}}{\text{volume of total solution}} \times 100 \quad (1-2)$$

Although units of mass or volume should always be expressed to avoid ambiguity, mass is usually implied when units are absent.

Confusing abbreviations:

mol – moles

M – molarity = $\frac{\text{mol solute}}{\text{L solution}}$

m – molality = $\frac{\text{mol solute}}{\text{kg solvent}}$

EXAMPLE Converting Weight Percent into Molarity and Molality

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{\text{g}}{\text{mL}}$$

A closely related dimensionless quantity is

$$\text{Specific gravity} = \frac{\text{density of a substance}}{\text{density of water at } 4^\circ\text{C}}$$

The density of water at 4°C is close to 1 g/mL, so specific gravity is nearly the same as density.

If you divide 1.01/0.063 0, you get 16.1. Dan got 16.1 because he kept all the digits in his calculator and did not round off until the end. The number 1.01 was really 1.014 8 and $(1.014 8)/(0.063 0) = 16.1$.

Find the molarity and molality of 37.0 wt% HCl. The density of a substance is the mass per unit volume. The table inside the back cover of this book tells us that the density of the reagent is 1.19 g/mL.

Solution For molarity, we need to find the moles of HCl per liter of solution. The mass of a liter of solution is $(1.19 \text{ g/mL})(1000 \text{ mL}) = 1.19 \times 10^3 \text{ g}$. The mass of HCl in a liter is

$$\text{Mass of HCl per liter} = \left(1.19 \times 10^3 \frac{\text{g solution}}{\text{L}}\right) \underbrace{\left(0.370 \frac{\text{g HCl}}{\text{g solution}}\right)}_{\substack{\text{This is what} \\ \text{37.0 wt% means}}} = 4.40 \times 10^2 \frac{\text{g HCl}}{\text{L}}$$

The molecular mass of HCl is 36.46 g/mol, so the molarity is

$$\text{Molarity} = \frac{\text{mol HCl}}{\text{L solution}} = \frac{4.40 \times 10^2 \frac{\text{g HCl}}{\text{L}}}{36.46 \frac{\text{g HCl}}{\text{mol}}} = 12.1 \frac{\text{mol}}{\text{L}} = 12.1 \text{ M}$$

For molality, we need to find the moles of HCl per kilogram of solvent (which is H_2O). The solution is 37.0 wt% HCl, so we know that 100.0 g of solution contains 37.0 g of HCl and $100.0 - 37.0 = 63.0 \text{ g}$ of H_2O ($= 0.063 \text{ kg}$). But 37.0 g of HCl contains $37.0 \text{ g}/(36.46 \text{ g/mol}) = 1.01 \text{ mol}$. The molality is therefore

$$\text{Molality} = \frac{\text{mol HCl}}{\text{kg of solvent}} = \frac{1.01 \text{ mol HCl}}{0.063 \text{ kg H}_2\text{O}} = 16.1 \text{ m}$$

Test Yourself Calculate the molarity and molality of 49.0 wt% HF, using the density given inside the back cover of this book. (Answer: 31.8 M, 48.0 m)

Figure 1-2 illustrates a weight percent measurement in the application of analytical chemistry to archaeology. Gold and silver are found together in nature. Dots in Figure 1-2 show the weight percent of gold in more than 1 300 silver coins minted over a 500-year period. Prior to A.D. 300, it was rare for the gold content to be below 0.3 wt%. By A.D. 600, people developed techniques for removing more gold from the silver, so some coins had as little as 0.02 wt% gold. Colored squares in Figure 1-2 represent known, modern forgeries made from silver whose gold content is always less than the prevailing gold content in the years A.D. 200 to 500. Chemical analysis makes it easy to detect the forgeries.

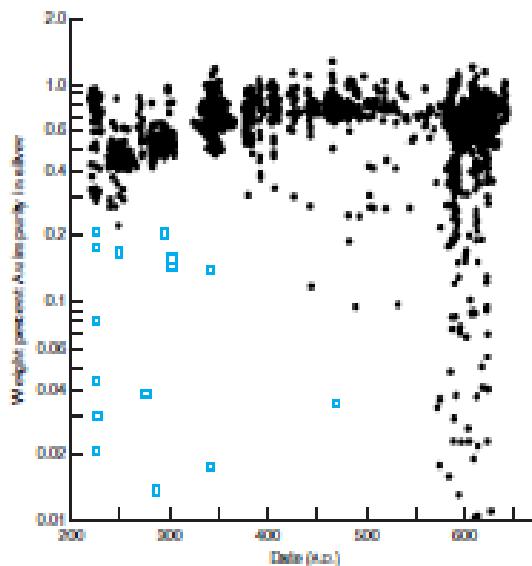


FIGURE 1-2 Weight percent of gold impurity in silver coins from Persia. Colored squares are known, modern forgeries. Note that the ordinate scale is logarithmic. [A. A. Cordis and I. P. Cordis, *Archaeological Chemistry*, *Adv. Chem.* No. 139, American Chemical Society, Washington, DC, 1974, pp. 124–147.]

Parts per Million and Parts per Billion

Sometimes composition is expressed as parts per million (ppm) or parts per billion (ppb), which mean grams of substance per million or billion grams of total solution or mixture. Because the density of a dilute aqueous solution is close to 1.00 g/mL, we frequently equate 1 g of water with 1 mL of water, although this equivalence is only approximate. Therefore, 1 ppm corresponds to 1 µg/mL (= 1 mg/L) and 1 ppb is 1 ng/mL (= 1 µg/L). For gases, ppm usually refers to volume rather than mass. Atmospheric CO₂ has a concentration near 380 ppm, which means 380 µL CO₂ per liter of air. It is best to label units to avoid confusion.

EXAMPLE Converting Parts per Billion into Molarity

Normal alkanes are hydrocarbons with the formula C_nH_{2n+2}. Plants selectively synthesize alkanes with an odd number of carbon atoms. The concentration of C₂₉H₆₀ in summer rainwater collected in Hannover, Germany is 34 ppb. Find the molarity of C₂₉H₆₀ and express the answer with a prefix from Table 1-3.

Solution A concentration of 34 ppb means there are 34 ng of C₂₉H₆₀ per gram of rainwater, a value that we equate to 34 ng/mL. Multiplying nanograms and milliliters by 1 000 gives 34 µg of C₂₉H₆₀ per liter of rainwater. The molecular mass of C₂₉H₆₀ is 408.8 g/mol, so the molarity is

$$\text{Molarity of C}_{29}\text{H}_{60} \text{ in rainwater} = \frac{34 \times 10^{-9} \text{ g/L}}{408.8 \text{ g/mol}} = 8.3 \times 10^{-9} \text{ M}$$

An appropriate prefix from Table 1-3 would be nano (n), which is a multiple of 10⁻⁹:

$$8.3 \times 10^{-9} \text{ M} \left(\frac{1 \text{ nM}}{10^{-9} \text{ M}} \right) = 83 \text{ nM}$$

$$\text{ppm} = \frac{\text{mass of substance}}{\text{mass of sample}} \times 10^6$$

$$\text{ppb} = \frac{\text{mass of substance}}{\text{mass of sample}} \times 10^9$$

Question What does one part per thousand mean?

Test Yourself How many ppm of C₂₉H₆₀ are in 23 µM C₂₉H₆₀? (Answer: 9.4 ppm)

nM = nanomoles per liter

1-3 Preparing Solutions

To prepare a solution with a desired molarity from a pure solid or liquid, we weigh out the correct mass of reagent and dissolve it in a volumetric flask (Figure 1-3).

EXAMPLE Preparing a Solution with a Desired Molarity

Copper(II) sulfate pentahydrate, CuSO₄ · 5H₂O, has 5 moles of H₂O for each mole of CuSO₄ in the solid crystal. The formula mass of CuSO₄ · 5H₂O (= CuSO₄H₁₀) is 249.68 g/mol. (Copper(II) sulfate without water in the crystal has the formula CuSO₄ and is said to be anhydrous.) How many grams of CuSO₄ · 5H₂O should be dissolved in a volume of 500.0 mL to make 8.00 mM Cu²⁺?

Solution An 8.00 mM solution contains 8.00×10^{-3} mol/L. We need

$$8.00 \times 10^{-3} \frac{\text{mol}}{\text{L}} \times 0.5000 \text{ L} = 4.00 \times 10^{-3} \text{ mol CuSO}_4 \cdot 5\text{H}_2\text{O}$$

The mass of reagent is $(4.00 \times 10^{-3} \text{ mol}) \times (249.68 \text{ g/mol}) = 0.999 \text{ g}$.

Using a volumetric flask: The procedure is to place 0.999 g of solid CuSO₄ · 5H₂O into a 500-mL volumetric flask, add about 400 mL of distilled water, and swirl to dissolve the reagent. Then dilute with distilled water up to the 500-mL mark and invert the flask several times to ensure complete mixing.

Test Yourself Find the formula mass of anhydrous CuSO₄. How many grams should be dissolved in 250.0 mL to make a 16.0 mM solution? (Answer: 139.61 g/mol, 0.638 g)



FIGURE 1-3 A volumetric flask contains a specified volume when the liquid level is adjusted to the middle of the mark in the thin neck of the flask. Use of this flask is described in Section 2-5.

Dilution

In Equation 1-3, you can use any units for concentration per unit volume (such as mmol/L or g/mL) and any units for volume (such as mL or μL), as long as you use the same units on both sides; we frequently use mL for volume.

Dilute solutions can be prepared from concentrated solutions. A volume of the concentrated solution is transferred to a fresh vessel and diluted to the desired final volume. The number of moles of reagent in V liters containing M moles per liter is the product $M \cdot V = \text{mol}/\text{L} \cdot \text{L}$, so we equate the number of moles in the concentrated (conc) and dilute (dil) solutions:

$$\underbrace{M_{\text{conc}} \cdot V_{\text{conc}}}_{\substack{\text{Moles taken from} \\ \text{concentrated solution}}} = \underbrace{M_{\text{dil}} \cdot V_{\text{dil}}}_{\substack{\text{Moles placed in} \\ \text{dilute solution}}} \quad (1-3)$$

EXAMPLE Preparing 0.100 M HCl

The molarity of "concentrated" HCl purchased for laboratory use is approximately 12.1 M. How many milliliters of this reagent should be diluted to 1.000 L to make 0.100 M HCl?

Solution The dilution formula handles this problem directly:

$$M_{\text{conc}} \cdot V_{\text{conc}} = M_{\text{dil}} \cdot V_{\text{dil}} \\ (12.1 \text{ M})(x \text{ mL}) = (0.100 \text{ M})(1.000 \text{ mL}) \Rightarrow x = 8.26 \text{ mL}$$

To make 0.100 M HCl, we would dilute 8.26 mL of concentrated HCl up to 1.000 L. The concentration will not be exactly 0.100 M because the reagent is not exactly 12.1 M. A table inside the cover of this book gives volumes of common reagents required to make 1.0 M solutions.

Test Yourself With information on the inside cover of the book, calculate how many mL of 70.4 wt% nitric acid should be diluted to 0.250 L to make 3.00 M HNO₃. (Answer: 47.5 mL)

EXAMPLE A More Complicated Dilution Calculation

A solution of ammonia in water is called "ammonium hydroxide" because of the equilibrium



The density of concentrated ammonium hydroxide, which contains 28.0 wt% NH₃, is 0.899 g/mL. What volume of this reagent should be diluted to 500.0 mL to make 0.250 M NH₃?

Solution To use Equation 1-3, we need to know the molarity of the concentrated reagent. The solution contains 0.899 g of solution per milliliter and there is 0.280 g of NH₃ per gram of solution (28.0 wt%), so we can write

$$\text{Molarity of NH}_3 = \frac{\frac{0.899 \text{ g solution}}{1 \text{ L}} \times 0.280 \frac{\text{g NH}_3}{\text{g solution}}}{17.03 \frac{\text{g NH}_3}{\text{mol NH}_3}} = 14.8 \text{ M}$$

Now we find the volume of 14.8 M NH₃ required to prepare 500.0 mL of 0.250 M NH₃:

$$M_{\text{conc}} \cdot V_{\text{conc}} = M_{\text{dil}} \cdot V_{\text{dil}} \\ 14.8 \text{ M} \times V_{\text{conc}} = 0.250 \text{ M} \times 500.0 \text{ mL} \Rightarrow V_{\text{conc}} = 8.46 \text{ mL}$$

The procedure is to place 8.46 mL of concentrated reagent in a 500-mL volumetric flask, add about 400 mL of water, and swirl to mix. Then dilute to exactly 500 mL with water and invert the flask many times to mix well.

Test Yourself From the density of 70.4 wt% HNO₃ on the inside cover, calculate the molarity of HNO₃. (Answer: 15.8 M)