1

The Metric System and Mathematical Tools

This chapter presents a review of mathematical concepts and procedures, as well as a concise summary of the metric system. In contrast to all other chapters in this book, which should be read in the order they are presented, this chapter can be skipped if you are familiar with the concepts or can be used to refresh certain aspects you may not have been exposed to. It is not recommended that you go through the entirety of Chapter 1 before you start working on the Chemistry sections, since many aspects of Chapter 1 are not needed until much later in the discussions.

1.1 Scientific Notation and Significant Figures

In science, one often has to deal with very large or very small numbers. Avogadro's number, given the symbol N_A in this text (see Section 2.4), is $N_A = 602214000000000000000000$. This representation is rather inconvenient and is written in scientific notation as $N_A = 6.02214 \cdot 10^{23}$. In general, numbers are written in scientific notation as

$$m \cdot 10^n \tag{1.1}$$

where n, the exponent, is a positive or negative integer number, and m, the mantissa, is $|-10| < m < 10$. Remember that $10^0 = 1$, $10^1 = 10$, $10^2 = 100$, $10^3 = 1000$, etc., and $10^{-1} = 0.1$, $10^{-2} = 0.01$, $10^{-3} = 0.001$, etc. Thus, in very small numbers, the exponent n is negative. The mass of a hydrogen atom, for example,

$$m_H = 0.0\ 000\ 000\ 000\ 000\ 000\ 000\ 000\ 016\ 735\ 575\ [g] \tag{1.2}$$

is presented in scientific notation as

$$m_H = 1.6735575 \cdot 10^{-24}\ [g] = 1.6735575 \cdot 10^{-27}\ [kg] \tag{1.3}$$

since 1 [g] = 10^{-3} [kg]. Eq. 1.3 introduced two further aspects: the metric system, to be reviewed in Section 1.2, and the manipulation of exponential expressions, discussed in Section 1.3.

Most scientific calculators abbreviate the exponential part, 10^n, as "En," for example, 10^2 appears as E2, or worse, as e+2. Do not confuse this with the number "e," Euler's constant (2.71828...), the basis of the natural logarithm that we will encounter in Section 1.3. So, when your calculator (or the calculator function in Windows) gives you a result "2.13158e-5," it is implied that it means $2.13158 \cdot 10^{-5}$. Also beware of a strange inconsistency in putting an exponential expression into the Windows calculator: the number 1000000, 1 million, or 10^6, must be entered as 1 followed by the "exp" key, followed by the number 6. If you enter 10 exp 6, it will read the number as 10000000. So BEWARE!!!

When you perform a numerical calculation, particularly with a calculator, you may be tempted to copy the result from the calculator without any further scrutiny. For example, if you are computing the circumference c of a circle with a radius r of 1.5 [cm], according to $c = 2\pi r$, your calculator will display 9.42477796076937971538793014983850 or something similar as an answer, if you use the value of π programmed into the calculator (you can, however, specify a different format). This answer implies that it is known to 32 significant figures. However, unless the radius is known to the same number of significant figures, the answer is worthless and misleading. When the radius is reported as 1.5 [cm], it implies that the next digit after the 5 is not known for sure: it could be 1.51 [cm], or 1.499 [cm], rounded down or up to 1.5 [cm]. This uncertainty results from the uncertainty in the measurement. If you use a simple ruler, 1.5 [cm] may be the best answer, given the graduation of the ruler. If you use a better measuring device, you may find that the radius is 1.514 [cm]. The accuracy

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of a measurement implies how close the measurement is to the true value. To indicate the improved accuracy of your measurement, you should report the radius as 1.514 [cm], with four significant figures.

If the calculation you are performing requires the radius to be entered in units of meters (see Section 1.2), with

$$1\ [\mathrm{cm}] = 10^{-2}\ [\mathrm{m}] \tag{1.4}$$

you retain the number of significant figures as follows:

$$r = 1.514 \cdot 10^{-2}\ [\mathrm{m}] \tag{1.5}$$

where as

$$r = 1.5 \cdot 10^{-2}\ [\mathrm{m}] \tag{1.6}$$

would imply the former situation with two significant figures. In any calculations, the input with the fewest significant figures determines with how many significant figures the results should be reported. Thus, the circumference should be reported as 9.4 [cm] in the first case above, and as 9.513 (9.5127 rounded to four significant figures) in the second case. Your main text most likely will have a number of examples. Most constants reported in this book are given with three or four significant digits although many are known to higher accuracy. As indicated, the number of significant figures is an indicator of the accuracy of a measurement.

When dealing with significant figures, notice that there are cases where a number occurs in an expression that has more significant figures than there are written. In the above example, $c = 2\pi r$, the number 2 is considered to be an exact number that is known to as many significant figures as necessary. This is, since the diameter and the radius of a circle are related by a factor exactly equal to 2.

1.2 The Metric System

The metric system of measurements is used in science, rather than the "imperial system" used predominantly in the English-speaking world. The metric system was introduced in France at the beginning of the nineteenth century with the aim of standardizing all measurements and providing reproducible standards. The unit of **length** in the metric system is the meter, abbreviated as [m], which is about 1.1 [yard]. The principle of the metric system is that all larger and smaller units (of length, in this case) are related to the meter by powers of 10. Thus, a kilometer [km] is 1000 [m], and a centimeter is 0.01 or 10^{-2} [m], unlike in the imperial system, where the conversion from miles to yards involves the factor of 1760, and from inches to yards by a factor of 36.

In the metric system, the powers of 10 for the conversion from larger to smaller (or vice versa) units are abbreviated as shown in Table 1.1 (notice that these abbreviations are case sensitive):

Table 1.1 Prefixes and abbreviations used in the metric system.

Factor	Prefix	Symbol
10^{15}	Peta	P
10^{12}	Tera	T
10^{9}	Giga	G
10^{6}	Mega	M
10^{3}	Kilo	k
10^{-2}	Centi	c
10^{-3}	Milli	m
10^{-6}	Micro	μ
10^{-9}	Nano	n
10^{-12}	Pico	p
10^{-15}	Femto	f

The conversion from centimeter to meter we encountered in Section 1.1

$$1.5\ [\text{cm}] = 1.5 \cdot 10^{-2}\ [\text{m}]$$

follows directly from the information in Table 1.1, since 1 [cm] = 10^{-2} [m]. For the reverse conversion, from meter to centimeter, we multiply both sides of Eq. 1.4 by 100, and obtain

$$1\ [\text{cm}] \cdot 10^2 = 10^{-2}\ [\text{m}] \cdot 10^2 \tag{1.4}$$

$$100\ [\text{cm}] = 1\ [\text{m}] \tag{1.7}$$

Area in the metric system is measured in units of [m^2]. Due to the ease of manipulating exponential expressions (see Section 1.3), the metric system affords easy conversion between, for example, [km^2] to [m^2]. Since 1 [km] = 10^3 [m], 1 [km^2] = $(10^3)^2$ [m^2] = 10^6 [m^2] = 1000000 [m^2]. It is easy to see why the metric system is superior to the imperial system, where a similar conversion, say from square mile to square feet, would require paper and pencil (or a calculator), since

$$1\ [\text{mile}] = 1760\ [\text{yards}] = 5280\ [\text{ft}] \tag{1.8}$$

$$1\ [\text{mile}^2] = 5280^2\ [\text{ft}^2] = 27\,878\,400\ [\text{ft}^2] \tag{1.9}$$

By the same logic, we can define **volumes** in the metric system: the volume is measured in units of [m^3]. The conversion factors shown in Table 1.1 have to be raised to the third power when converting volumes, for example, 1 [cm^3] = $(10^{-2})^3$ [m^3] = 10^{-6} [m^3] = 0.000 001 [m^3]. The volume V of a cube 10 [cm] on edge would be

$$V = (10\ [\text{cm}])^3 = 10^3\ [\text{cm}^3] = 1000\ [\text{cm}^3] \tag{1.10}$$

is also called 1 liter [L]. Consequently,

$$1\ [\text{mL}] = 1\ [\text{cm}^3] \tag{1.11}$$

Mass originally was defined in units of gram [g], where the mass of 1 [cm^3] = 1 [mL] of water is 1 [g], or the mass of 1 [L] of water is 1 [kg]. This was based on the definition of the density (see next paragraph) of water to be 1 [g/mL]. The units discussed so far have been redefined to much higher accuracy and reproducibility, but in the context of this book, the old definitions are sufficiently accurate.

Many units are derived from these basic units. **Density d,** for example, is defined as the ratio of mass over volume:

$$d = m/V \tag{1.12}$$

Water, as mentioned above, has a density of 1 [g/mL]. Mercury, a very dense (and liquid) metal, has a density of 13.6 [g/mL] or 13.6 [kg/L]. So, if you are asked what volume of mercury will have a mass of 1.00 [g], you would solve the definition of density for the volume,

$$V = m/d = 1.00/13.6 = 0.0735 = 7.34 \cdot 10^{-2}\left[\frac{\text{g}}{\frac{\text{g}}{\text{mL}}} = \text{mL}\right] \tag{1.13}$$

Force (mass · acceleration) has units of [kg m/s^2] = 1[N] (Newton), and **energy** has units of force · distance or [Nm] = [kg m^2/s^2] = [J] (Joule, see below).

Temperature, in the metric system, is reported on the Celsius scale in degrees centigrade [°C]. It was originally defined by two limiting temperatures: the ice/water equilibrium mixture was defined to have a temperature of 0 [°C], and the water boiling temperature was defined as 100 [°C] (at an ambient pressure of 1 [atm], see below). These two experimental conditions can be readily reproduced allowing easy calibration of thermometers worldwide. However, as shown in the discussion of the gaseous state (Chapter 8), it becomes clear that the centigrade scale is as arbitrary as other temperature scales (for example, the Fahrenheit scale used in the United States), and another temperature scale needed to be defined. In this new temperature scale, the zero point is not defined arbitrarily, but based on the concept that an ideal gas approaches zero pressure (or zero volume) when the temperature is zero degrees on a new scale. This is due to the fact that the pressure p depends on the temperature as given by the ideal gas law

$$p = \frac{nR}{V}T \tag{1.14}$$

(see Eq. 8.14). Thus, the temperature has to be defined such that p is zero as T is zero. The temperature zero point can be obtained by extrapolating the p,T diagram shown in Figure 1.1 to zero pressure. In this temperature scale, known as the Kelvin (K) temperature, the size of the increment is the same in the centigrade and the Kelvin scale, 1 [K] = 1 [°C]. Hence,

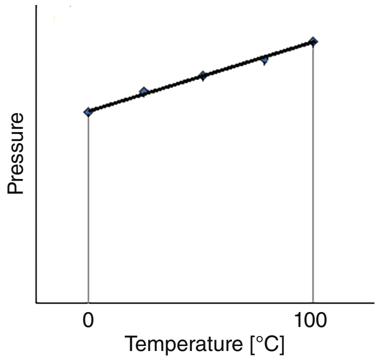

Figure 1.1 Plot of ideal gas pressure vs. temperature in [°C].

we are allowed to use [°C] units in calorimeter (Section 11.2.2) since we discuss temperature changes in this section.

The zero point of the Kelvin temperature scale is found to be $T_K = -273.16$ [°C]. For temperature conversions, the following equations are useful:

$$T_F = 1.8\ T_C + 32 \tag{1.15}$$

$$T_K = T_C + 273 \tag{1.16}$$

Here, T_C denotes temperature in centigrade units, T_F in Fahrenheit units, and T_K in Kelvin units. In section 1.4, a few examples of temperature conversions will be discussed.

Pressure is defined as force per unit area, and thus, the pressure units in the metric system are Newton per square meter [N/m^2] = 1 [Pa] (Pascal). However, in this book, and in most Chemistry texts, the older definition, based on the atmospheric pressure of the earth's atmosphere, is used. Here,

$$1\ [\text{atm}] = 760\ [\text{mm Hg}] = 101,325\ [\text{Pa}] \tag{1.17}$$

As we shall see in the section on Thermochemistry (Section 11.2), **heat** is a form of energy, and consequently, has units of energy. Originally the unit of heat was defined in the metric system as the amount of heat required to raise the temperature of 1 [g] = 1 [mL] of water by 1 [°C]. This amount of heat was called 1 calorie [cal]. In modern scientific work, the calorie has been replaced by the metric unit of energy: 1 [cal] = 4.18 [J]. This unit of heat, and its multiple, 1 [kJ] = 1000 [J] is used throughout this book. Interestingly, the unit [cal] is still used in nutritional science and sports medicine; however, it is used incorrectly. What a nutritionist calls 1 [cal] is actually 1 [kcal]; thus, if a paper in sports medicine reports the base metabolic rate of an adults as 2000 [cal], it actually implies 2000 [kcal].

Time, the unit of which in both the metric and imperial system is the second [s], uses the same prefixes for fractions of a second: 1 [ms] = 10^{-3} [s], 1 [ns] = 10^{-9} [s], etc. However, for time periods larger than 1 [s], we use minutes and hours, rather than kiloseconds (you see here that there are a few inconsistencies in the metric system as well). This has mostly historical reasons, since we are accustomed to a day's length as 24 [h], with 1 [h] = 3600 [s], and one year as 365 days. The latter time units (days, years) are relevant in Chapters 13 and 14, where we deal with the half-lives of very slow reactions. By the way, ignore the occurrence of leap years (with 366 days/year) in these calculations, since the few extra days do not matter, within the significant figures, if a half-life is given as 240 000 years (see Figure 14.1).

1.3 Manipulations of Exponential Expressions

Addition/subtraction of exponential expressions: ascertain that the exponents are the same, then proceed by adding the mantissa.

Examples:

$$1.20 \cdot 10^{12} + 2.3 \cdot 10^{11} = 1.20 \cdot 10^{12} + 0.23 \cdot 10^{12} = 1.43 \cdot 10^{12} \quad \text{(three significant figures)} \tag{1.18}$$

$$1.20 \cdot 10^{-12} - 2.3 \cdot 10^{-11} = 0.12 \cdot 10^{-11} - 2.3 \cdot 10^{-11} = -2.2 \cdot 10^{-11} \quad \text{(two significant figures)} \tag{1.19}$$

Multiplication/division of exponential expressions:

$$a^n \cdot a^m = a^{(n+m)};\ a^n/a^m = a^{(n-m)};\ (a^n)^2 = a^{2n} \tag{1.20}$$

Examples:

$$10^{20} \cdot 10^3 = 10^{23}; 10^{20}/10^3 = 10^{17} \tag{1.21}$$

$$6.3 \cdot 10^3 \cdot 4.5 \cdot 10^5 = 6.3 \cdot 4.5 \cdot 10^8 = 28.35 \cdot 10^8 = 2.8 \cdot 10^9 \quad \text{(two significant figures)} \tag{1.22}$$

To experience a typical computation involving exponential expressions, we turn to a calculation from Chapter 15 (Example 15.3):

$$\frac{\left(6.6 \cdot 10^{-34}\right)^2}{8 \cdot 9.1 \cdot 10^{-31} \cdot (10^{-9})^2} = \frac{(6.6)^2}{8 \cdot 9.1}\frac{10^{-68}}{10^{-49}} = \frac{43.56}{72.8} \cdot 10^{-19} = 0.598 \cdot 10^{-19} = 6.0 \cdot 10^{-20} \quad \text{(two significant figures)} \tag{1.23}$$

When using an electronic calculator, not all intermediate steps shown above are necessary, and the fraction $\frac{(6.6 \cdot 10^{-34})^2}{8 \cdot 9.1 \cdot 10^{-31} \cdot (10^{-9})^2}$ could have been entered directly into the calculator. However, the step $\frac{43.56}{72.8} \cdot 10^{-19}$ was added since it allows you to estimate, in your head, the order of magnitude of the result. Thus, if you enter any number incorrectly into your calculator, this step allows you to verify the result you get from the calculator. Notice also that the number "8" in the denominator is an exact number, so it does not influence the number of significant figures.

1.4 Equations, Proportionality, and Graphs

The **proportionality** expresses the dependence of a variable (the "dependent" variable) on another variable referred to as the independent variable. The independent can assume any value, whereas the dependent variable can assume only values given by the proportionality. The circumference C of a circle, for example, is proportional to the diameter d of the circle according to:

$$C \propto d \tag{1.24}$$

Any proportionality can be written as an equation by inserting a proportionality constant:

$$C = \pi \cdot d \tag{1.25}$$

where the proportionality constant is π. A plot of c, the dependent variable, vs. d (the independent variable), gives a straight line with the slope of 3.14159.

In general, any proportionality can be written as an equation, and we have made use of this statement many times in the text of the book. An equation can be solved for either of the variables by straightforward algebraic manipulations, as long as the manipulation is applied to both sides of the equation (with the exception of division by zero, which is a no-no). Let us take the relationship between temperature, expressed in degrees Fahrenheit (T_F), and in centigrade scale (T_C) for an example. This relationship is

$$T_F = 1.8\ T_C + 32 \tag{1.15}$$

What does an equation like Eq. 1.15 tell us? First of all, it tells us that the dependence of T_F is linear with T_C. You may ascertain that this equation is correct by inserting temperature values with known outcome: the boiling temperature of water in the centigrade scale, $T_C = 100$ [°C], when inserted into Eq. 1.15, correctly results in the boiling temperature of water as $T_F = 212$ [°F]. Now, if a temperature is given in [°F] and you want to express it in [°C], use a little algebra and get

$$1.8\ T_C = T_F - 32 \quad \text{or} \quad T_C = (T_F - 32)/1.8 \tag{1.26}$$

For example, a cold morning with a temperature of −4 [°F] would have registered as −20 [°C] on a thermometer calibrated in centigrade units. I would recommend not to memorize both Eqs. 1.15 and 1.26 (because the storage space in your brain is limited) but rather, memorize one, say Eq. 1.15, and derive the other form as needed.

This last statement is even more important when you have an equation that contains more than two variables. Take the ideal gas law (see Chapter 8),

$$p\,V = n\,R\,T \tag{8.14}$$

Here, p, V, n, and T are all variables, and only R is a constant (hence the name "gas constant"). If you wish to visualize how the volume of a gas depends on its pressure (keeping the temperature and amount of gas constant), you would write

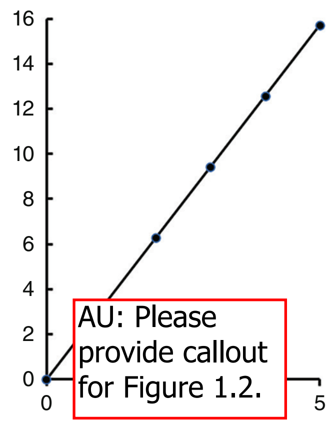

Figure 1.2 Dependence of a circle's circumference on diameter.

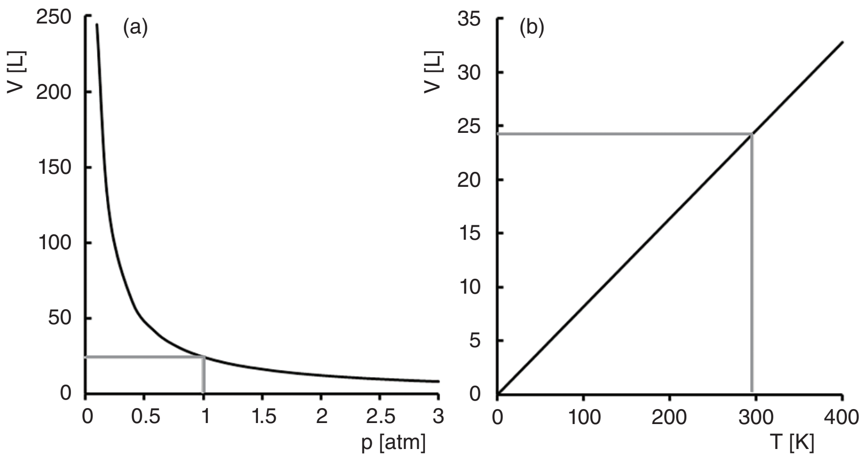

Figure 1.3 (a) Plot of gas volume vs. pressure at constant temperature, 298 [K]. The gray lines denote the volume of 1 mole of gas, V = 24.2 [L] at 298 [K]. (b) Plot of gas volume vs. temperature at constant pressure, 1 [atm]. The gray lines denote the volume of 1 mole of gas, V = 24.2 [L] at 1 [atm] pressure.

$$V = nRT \frac{1}{p} \quad (1.27)$$

$$\text{which implies} \quad V \propto 1/p \quad (1.28)$$

If you use 1.00 [mol] of an ideal gas at 298 [K] (do not forget, always use Kelvin temperatures), you get a plot shown in Figure 1.3a. The shape of this curve is a hyperbola, as expected from the inverse proportionality. If you wish to visualize how the volume of a gas depends on temperature (keeping the pressure and amount of gas constant), you would write

$$V = \frac{nR}{p} T \quad (1.29)$$

$$\text{or} \quad V \propto T \quad (1.30)$$

which is shown in Figure 1.3b.

The take home point from this discussion is that in a scientific equation such as the ideal gas law, the same rules apply that you have learned in algebra classes, and that simply solving the equation for the unknown (by algebraic rules) allows you to predict the functionality, and the shape of plots you obtain. When any of the variables appear in the second or third power, we have to revert to different methods to solve for the allowed numerical values. This will be discussed in Section 1.5.

Eq. 1.26 was written as a function that relates two variables – depending which way they are written – either temperature can be the dependent or independent variable. Let us now look at another situation (a common question in general chemistry exams), namely "is there a temperature where the numeric values of the Fahrenheit and centigrade scale are equal?" Since the relationship of the two scales is given by

$$T_F = 1.8\ T_C + 32 \quad (1.15)$$

we need to find a temperature for which

$$T_F = T_C \quad (1.31)$$

that is, we have two equations that need to be solved together. In algebra class of earlier years, you would have encountered the same problem written as

$$y = a\,x + b \quad (1.32)$$

$$\text{and} \quad y = x. \quad (1.33)$$

Then, you would have substituted Eq. 1.33 into Eq. 1.32 to obtain $x = a\,x + b$, and solved for x

$$\text{to get P } x = b/(1 - a) \quad (1.34)$$

Applying the same approach to the pair of Eqs. 1.15 and 1.31 gives the temperature for which Eq. 1.31 holds as

$$T = -40\ [°F]\ \text{or}\ [°C] \quad (1.35)$$

where the numerical values of T_F and T_C are the same. You also could graph the two functions and search for their intersect. This is shown in Figure 1.4. Here, the black line shows the Fahrenheit temperature as a function of the centigrade temperature. As you can see, the slope is larger than 1 (in fact, 1.8), and it intersects the y-axis at 32, as expected. The gray line is a plot of the centigrade temperature vs. itself; therefore, we get a line with a slope of one and a zero intersect. Finally, we see that the lines intersect at −40 [°C], as calculated by Eq. 1.35.] By the arguments shown above, think about the following two questions:

(1) At what temperature does the Fahrenheit temperature intersect the abscissa? (In other words, at what centigrade temperature is the Fahrenheit temperature 0?)
(2) Is there a temperature where the centigrade and Kelvin scale have the same numerical value?

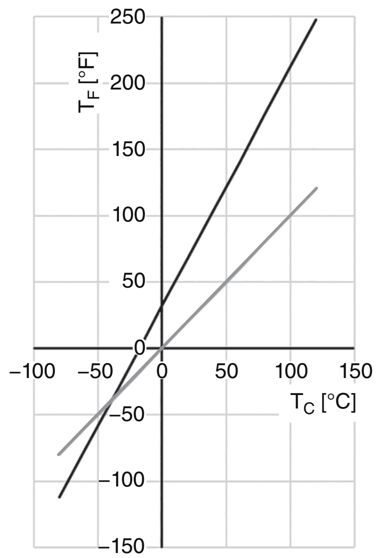

Figure 1.4 Lot of centigrade and Fahrenheit temperature scales.

1.5 Quadratic, Cubic, and Quartic Equations

Quadratic equations are equations in which the variable occurs to the second power, or the first and second power. Here, we consider two cases.

Case 1: the variable occurs to the second power only:

$$x^2 - a = 0, \quad \text{or} \quad x^2 = a; \tag{1.36}$$

The equation has two solutions x_+ and x_- given by

$$x_{+,-} = \pm\sqrt{a} \tag{1.37}$$

Example: The area A of a circle is given by $A = \pi r^2$. Let the area of a circle be 200 [cm]^2. What is the radius of the circle? $A = \pi r^2$; $r^2 = A/\pi$; $r = \pm\sqrt{200/\pi} = \pm 7.98$ [cm]. Here, only the positive answer makes sense.

Case 2: the variable occurs to the second and first power:

$$ax^2 + bx + c = 0 \tag{1.38}$$

This equation has two solutions x_+ and x_- given by

$$x_+ = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad \text{and} \quad x_+ = \frac{-b - \sqrt{b^2 - 4ac}}{2a} \tag{1.39}$$

This is generally written as $x_{+,-} = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Example: (from Chapter 10, Eq. 10.25)

$$x^2 + 7.2 \cdot 10^{-4} \times -7.2 \cdot 10^{-6} = 0$$

Here, $a = 1$, $b = 7.2 \cdot 10^{-4}$, $c = -7.2 \cdot 10^{-6}$

$$x_{+,-} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-7.2 \cdot 10^{-4} \pm \sqrt{(7.2 \cdot 10^{-4})^2 - 4 \cdot 1 \cdot (-7.2 \cdot 10^{-6})}}{2} \tag{1.40}$$

Notice that in real applications such as general equilibrium calculations, the radical (the part under the square root symbol) must be positive. If it is not, you – most likely – have made a mistake with the sign (remember, it is −4ac)

$$x_{+,-} = \frac{-7.2 \cdot 10^{-4} \pm 5.415 \cdot 10^{-3}}{2} \tag{1.41}$$

$$x_+ = 2.34703 \cdot 10^{-3} \tag{1.42}$$

$$x_- < 0 \tag{1.43}$$

Which of the two solutions of a quadratic equation is physically meaningful often cannot be determined from the mathematical view but has to be decided based on the conditions. The result for x_- (Eq. 1.43), for example, is negative, but a negative concentration is physically not meaningful.

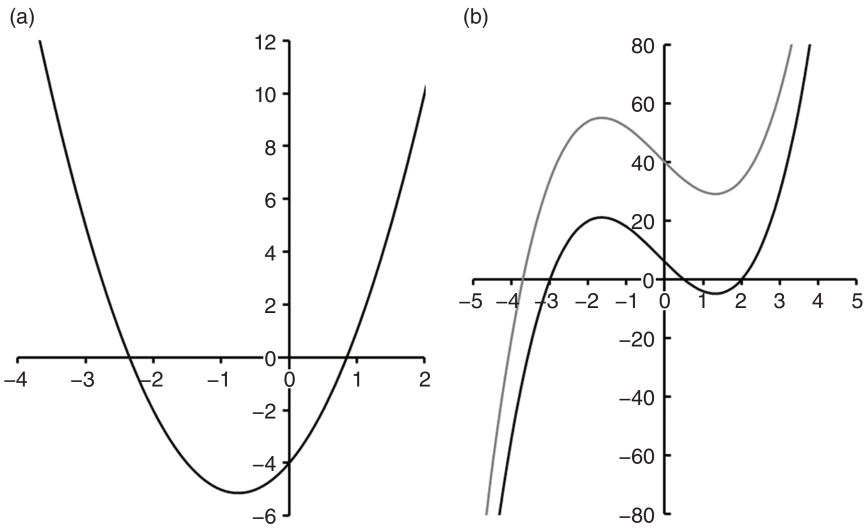

Figure 1.5 Graphic solution of (a) a quadratic equation and (b) a cubic equation.

The expression $f(x) = ax^2 + bx + c$ that we encountered in Eq. 1.38 actually is what we call a polynomial (see Eq. 5.21) in the single variable x. Such polynomials also can be solved for x graphically by plotting the function f(x) and searching for the intersections of the functions with the abscissa, at which f(x) is zero. Consider the function $f(x) = 2x^2 + 3x - 4$. The plot of this function is shown in Figure 1.5a with the two abscissa intersects at −2.35 and +0.85, corresponding to the numerical values you would obtain if you substituted a = 2, b = 3, and c = −4 into Eq. 1.39.

The graphical method outlined above can be used to solve cubic (or higher) equations as well. For cubic equations (polynomials) of the form $f(x) = ax^3 + bx^2 + cx + d$, there is no simple solution corresponding to Eq. 1.39, and the graphical approach can show how many real solutions exist. This is shown in Figure 1.5b (black trace), which depicts the function $f(x) = 2x^3 + x^2 - 13x + 6$. This function has roots (solutions) at x = 2, x = 0.5, and x = −3. Once one root is known, for example x = 2, we can divide the original function f(x) by (x − 2), if we exclude x = 2 in the division (since that would be a disallowed division by zero). This step reduces the cubic equation to a quadratic equation, since

$$\left(2x^3 + x^2 - 13x + 6\right)/(x - 2) = 2x^2 + 5x - 3 \quad (\text{for } x \neq 2) \tag{1.44}$$

The quadratic equation $2x^2 + 5x - 3 = 0$ has roots of 0.5 and −3, as shown in Figure 1.5b. Notice that the same function offset along the y-axis, that is $f(x) = 2x^3 + x^2 - 13x + 40$ (Figure 1.5b, gray trace) has only one solution.

Quartic equations have the variable at up to the fourth power. In the context of this book, we encountered quartic equations in equilibrium calculations. Fortunately, they contained only even powers of x, such as

$$ax^4 + bx^2 + c = 0 \tag{1.45}$$

which can be solved by successive application of the quadratic equation approach.

1.6 Exponential Functions and Logarithms

In Section 1.3, we have dealt with numbers that have exponential expressions and have learned how to manipulate them. Next, we will take a look at functions that have the variable x in the exponent, such as the functions

$$y = 10^x \quad \text{or} \quad y = e^x \tag{1.46}$$

You may or may not have encountered functions of this kind in high school algebra; thus, it is necessary to spend some time here and explain where these functions are coming from. The most tangible way to explain these "growth functions" is as follows. Imagine you put US\$1.00 into a bank account that rewards you with 5% interest, compounded yearly. So, after one year, you find US\$1.05 in your account. After two years, the interest was calculated for the new starting amount in your account, so the interest earned in the second year is $1.05 \cdot 0.05 = 0.0525$, which is added to your balance after the second year. Your balance after the second year, therefore, is US\$1.1025. If you keep the funds in the account, they will grow according to

$$(1 + 1 \cdot 0.05)^x \tag{1.47}$$

where x is the number of years. There are several interesting aspects to Eq. 1.47. First, the growth function given by Eq. 1.47 is shown by the gray trace in Figure 1.6 and indicates that after 60 years, your US$1 investment would have grown to 18 bucks. Not bad for doing nothing (imagine what would have happened if you had invested US$10 000?). Second, the factor 0.05, of course, is the interest rate of 5%. Even at a moderately larger interest rate of 7.5%, your capital would have grown much faster, to US$64.5 in 60 years. Finally, if the interest was not compounded yearly, but monthly, daily, or even hourly, your capital would have grown slightly faster than at the yearly rate. This is shown by the black trace in Figure 1.6, which is for infinitesimally short time increments, or a growth function where the compounding period approaches zero. This is known as the natural growth function, $y = e^{ax}$. Here, e (represented by a script letter "e" to distinguish it from the electronic charge, e) is Euler's number, which, like π, is an irrational number with a numerical value

$$e \approx 2.71828\ \ldots \tag{1.48}$$

and is known as the basis of natural growth, as we have seen in the example of our investment scheme above. The value of e itself is defined as a growth function:

$$e = \lim_{n\to\infty}\left(1 + \frac{1}{n}\right)^n \tag{1.49}$$

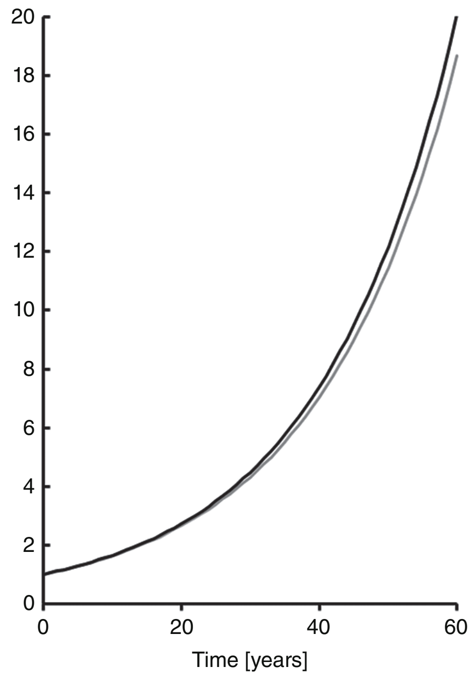

Figure 1.6 Growth functions. Black trace: $e^{0.05x}$; gray trace $(1 + 1 \cdot 0.05)^x$.

Since it is easier for us to use powers of 10, rather than powers of e (after all, we all know what 10^3 is, but who knows what e^3 is?), we often convert powers of e to powers of 10 according to

$$10^x = e^{2.303x} \tag{1.50}$$

$$\text{since} \quad e^{2.303} \approx 10 \tag{1.51}$$

Although the conversion from powers of e to powers of 10 is useful, I suggest that you get familiar with the e^{ax} and e^{-ax} functions on your calculator, since they (and their inverse function, the logarithm functions) occur frequently in Chapters 9 and 14.

While we call the function $y = e^{ax}$ the natural growth function, the function $y = e^{-ax}$ is referred to as the natural decay function. A plot of both exponential functions is presented in Figure 1.7. The natural decay function predicts, for example, the decay in concentration of medication in the bloodstream with time, or the amount of an element left over after it undergoes radioactive decay. Examples of such calculations are found after the discussion of logarithms.

The inverse mathematical operations of exponential functions are logarithmic functions. Logarithms occur in the text of this book in several places (Chapter 7 in the discussion of vapor pressure, Chapter 10 in the discussion of pH and pOH, and in Chapter 14 in the discussion of reaction rates). A logarithm is the exponent to which a base must be raised to yield a given number. For example, the equation

$$10^x = 2 \tag{1.52}$$

has a solution

$$x = \log 2 \approx 0.3010\ldots \tag{1.53}$$

In other words, taking the logarithm is the inverse operation to exponentiation. Log 2 could have been written as $\log_{10}2$ to indicate the base 10. However, in this book, the symbol "log" always will indicate base 10.

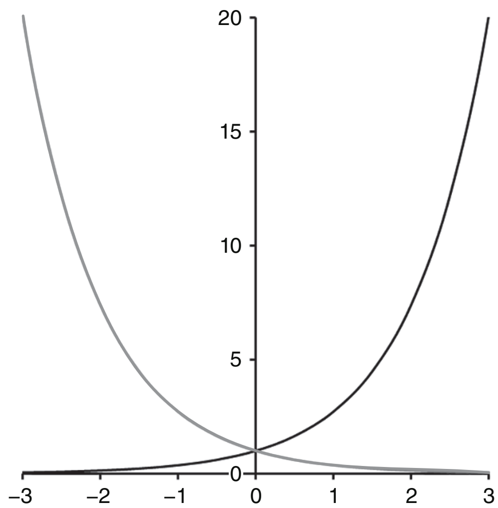

Figure 1.7 Plot of $y = e^x$ (black trace) and $y = e^{-x}$ (gray trace).

Remembering Eq. 1.20:
$10^n \cdot 10^m = 10^{(n+m)}$ and $\log 2 = 0.3010$, we see that the logarithm of

$$\begin{aligned} &\log 20 = \log(10 \cdot 2) = \log 10 + \log 2 = 1.3010 \text{ and} \\ &\log 200 = \log 100 + \log 2 = 2.3010. \end{aligned} \tag{1.54}$$

It also follows that

$$\log(0.2) = \log(10^{-1}) + \log 2 = -0.6990 \tag{1.55}$$

When taking the logarithm of an exponential expression, such as 2^x, the exponent becomes a factor:

$$\log(2^x) = x \log(2) \tag{1.56}$$

In many calculations in the text, the natural logarithm, rather than the decadic logarithm, is used. The natural logarithm (called the "ln" function in this book) is the exponent to which the number *e* must be raised to yield a given number. For example, the equation

$$e^x = 2 \tag{1.57}$$

$$\text{with } x = \ln 2 \approx 0.693 \tag{1.58}$$

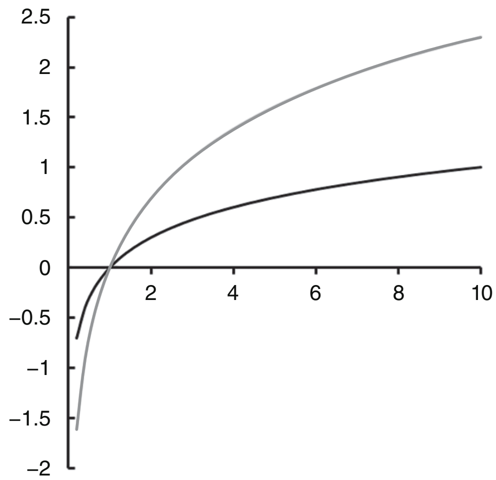

Figure 1.8 Plot of the log x (black) and ln x (gray) functions.

The prevalence of natural logarithm and natural growth functions in Chemistry arises because the integral

$$\int_{x_a}^{x_b} \frac{1}{x}\, dx = \ln\frac{x_b}{x_a} = \ln(x_b) - \ln(x_a) \tag{1.59}$$

is given by the ratio of the natural logarithm of the two values between which the integration is carried out, x_b and x_b. This integral occurs frequently in the derivation of equations such as the first-order rate law in kinetics, and other places, and will be discussed in more detail in Section 1.8. A graph of the log x and ln x functions is shown in Figure 1.8.

We now turn to a number of examples from the main text to practice exponential and logarithmic functions.

Example 10.3 Calculate the pH of a 1.5 [M] aqueous solution of HCl.

Answer: $\text{pH} = -\log[H^+] = -\log(1.5) = -(0.1761) = -0.18$ (1.60)

This example is discussed here, although it seems very easy and straightforward, to indicate an issue with significant figures in exponential calculations. The result in Eq. 1.60 was rounded to two significant figures, which is appropriate for the problem as stated. If we want to check out our calculation, we would use the reverse of the logarithm function, the "anti-log" function. The anti-log $(0.18) = 10^{0.18} = 1.513$. Here, we see a feature commonly encountered in exponential and logarithmic manipulations: the result in Eq. 1.60 was recorded to the correct number of significant figures. The reverse calculation, however, gave a different result. Therefore, it is advisable to perform intermediate calculations with more significant figures in logarithmic calculations. In the example above, the difference between the original concentration (1.5[M]) and the recalculated concentration of 1.513 [M] is due to truncation of the pH to two significant figures. If the pH is reported as pH = −0.1761, then $10^{0.1761}$ gives a more satisfactory result of 1.5000.

Example 9.2 Use the enthalpy of vaporization of butane, 22.4 [kJ/mol], and its vapor pressure at 298 [K], 2.41 [atm], to calculate the vapor pressure of butane at 473 [K] (this problem is solved in Example 9.2 using the logarithmic approach. Here, it is solved using the corresponding exponential equations):

$$\frac{p_{473}}{p_{298}} = e^{\frac{\Delta H_{vap}}{R}\left(\frac{1}{298} - \frac{1}{478}\right)}, \text{ or } p_{473} = p_{298}\ e^{\frac{22{,}400}{R}\left(\frac{1}{298} - \frac{1}{473}\right)} \text{ with } R = 8.3[\text{J/(K mol)}]$$

$$p_{473} = 2.41\ e^{2698.8\,(0.0033557-0.0021142)}$$

$$p_{473} = 2.41\ e^{2698.8\,(0.0012415)} = 2.41\ e^{3.35066} = 2.41 \cdot 28.52 = 68.7\ [\text{atm}].$$

Example 13.2 Consider an elementary step A → C with a rate constant $k = 0.3\ [s^{-1}]$. Calculate the ratio $[A]_o/[A]_t$ after 10 s.

Answer: $\log \frac{[A]_0}{[A]_t} = k\ t/2.303 = 0.3 \cdot 10/2.303\left[s^{-1} s\right] = 1.3026;$

$$\frac{[A]_0}{[A]_{10}} = \text{antilog}\ (1.3026) = 20.1;\ [A]_{10} \approx \frac{[A]_0}{20}$$

1.7 Radial and Spherical Polar Coordinates

When plotting functions as discussed in Sections 1.4–1.6, we define a point in a plane by its x and y coordinates, as shown in Figure 1.9a. The same point in a plane can also be described in polar coordinates by its distance from the origin, given by the vector **r**, and the angle φ between the vector **r** and the positive X-axis, with $0 < \varphi < 2\pi$, or $0 < \varphi < 360°$ (Figure 1.9b).

The decision on which of the two coordinate systems to use often is dictated by the problem itself: the particle-in-a-square-box was described previously in Cartesian coordinates (see Figure 15.3 in Chapter 15), whereas the particle-in-a-circular-box was presented in polar coordinates (see Figure 15.4 in Chapter 15) due to the different shapes and symmetries of the confinements.

Using our knowledge of trigonometry, we find that the two coordinate systems can be related to each other by

$$x = r \cos \varphi \tag{1.61}$$

$$y = r \sin \varphi \tag{1.62}$$

Since $x^2 = r^2 \cos^2 \varphi$ and $y^2 = r^2 \sin^2 \varphi$, it follows that

$$x^2 + y^2 = r^2 \cos^2 \varphi + r^2 \sin^2 \varphi = r^2 \left(\cos^2 \varphi + \sin^2 \varphi\right) = r^2 \quad \text{since} \quad \cos^2 \varphi + \sin^2 \varphi = 1$$

$$\text{The equation } x^2 + y^2 = r^2 \tag{1.63}$$

describes a circle with radius r, located at the center of the coordinate system. This leads to the polar equation r(φ) of a circle at the center of the coordinate system:

$$r(\varphi) = a \tag{1.64}$$

where the constant a is just the radius of the circle. This is an important aspect, as we shall see below (Eq. 1.69).

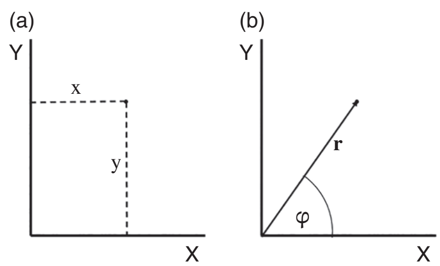

Figure 1.9 Cartesian (a) and polar (b) coordinates.

In three-dimensional space, we define the spherical polar coordinates (rather than polar coordinates introduced above) for a point with Cartesian coordinates x, y, and z in terms of the variables r, θ, and φ as shown in Figure 1.10. The angle θ is measured between the line OP and the positive z-axis and runs from +90 to −90 degrees $\{-\pi/2$ to $\pi/2\}$, just as the latitude of a point on earth. The other angle, φ, is defined between the positive x-axis and the projection of OP onto the x–y plane, and runs between 0 and 2π. This angle corresponds to the longitude of a point on earth. The coordinates x, y, z of an arbitrary point in space are described in polar coordinates as

$$x = r \sin \theta \cos \varphi \tag{1.65}$$

$$y = r \sin \theta \sin \varphi \tag{1.66}$$

$$z = r \cos \theta \tag{1.67}$$

In analogy to Eq. 1.63, the equation

$$x^2 + y^2 + z^2 = r^2 \tag{1.68}$$

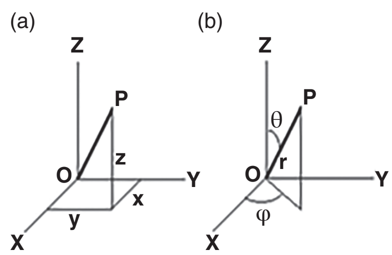

Figure 1.10 Cartesian (a) and spherical polar (b) coordinates.

describes a sphere with radius r, located at the center of the coordinate system. In polar coordinates φ and θ, the equation of a sphere is

$$r(\varphi,\theta) = a \tag{1.69}$$

in analogy to Eq. 1.64, where a is the radius of the sphere. This explains a statement earlier in Section 15.2 that the spherical harmonic function $Y_0^0 = Y(\varphi,\theta) = \frac{1}{2}\sqrt{\frac{1}{\pi}}$ (Eq. 15.18) represents a sphere.

Section 15.2 also pointed out that the second derivative of a function, given in Cartesian coordinates, $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, becomes a scary-looking

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\ \sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{r^2\ \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) \tag{15.13}$$

in spherical polar coordinates.

1.8 Differential and Integral Calculus

Differential calculus is a branch of mathematics dealing with the slope, or the rate of change, of a function. This is understood best by considering the graph in Figure 1.11. Here, we have a function, $f(x) = x^2$, plotted vs. x. The slope of the function f(x) at x = 1 (heavy black line in Figure 1.11) can be determined as follows. If we draw a secant from the point (x = 4, y = 16) to the point (x = 1, y = 1), we get a slope S_a of this line as $S_a = \Delta y/\Delta x = 15/3 = 5$. The secant from point x = 3, y = 9 to the point (x = 1, y = 1) has a slope of $S_b = 8/2 = 4$. Finally, the slope of secant "c" is $S_c = 3/1 = 3$. If we let Δx get infinitesimally small, the slope at point x = 1, y = 1 (which is a tangent, rather than a secant) becomes 2. If we repeat the same approach for other points along the $f(x) = x^2$ curve, we find that the slope of this function is 2x at any point. We then define the slope of the function f(x) for infinitesimally small values of dx, as the derivative, $\frac{df(x)}{dx} = \frac{dx^2}{dx} = 2x$. For any function of the form $f(x) = a\,x^b$, the derivative is given by

$$\frac{df(x)}{dx} = (ab)\,x^{b-1} \tag{1.70}$$

Thus, the derivative of the function $f(x) = x^2$ is $\frac{d}{dx}f(x) = \frac{d}{dx}(x^2) = 2x$, and the derivative of the function $f(x) = 4x^3$ is $\frac{d}{dx}f(x) = \frac{d}{dx}(4x^3) = 12x^2$.

The derivatives of trigonometric functions are very important for our discussion:

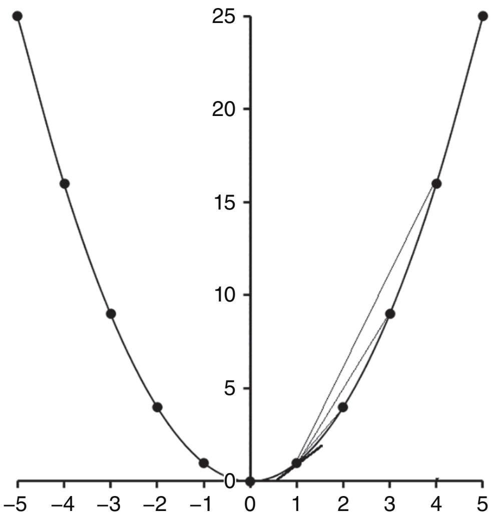

Figure 1.11 Slope of an algebraic function.

$$\frac{d\ \sin(ax)}{dx} = a\cos(ax) \quad \text{and} \quad \frac{d\ \cos(ax)}{dx} = -a\sin(ax) \tag{1.71}$$

Furthermore, $$\frac{d\,e^{ax}}{dx} = a\,e^{ax} \tag{1.72}$$

Taken derivatives of a function successively leads to the second derivative, $\frac{d^2 f(x)}{dx^2}$. In physics, you may have encountered that velocity is defined as the derivative of the position with respect to time,

$$v = \frac{dx}{dt} \tag{1.73}$$

and acceleration a as the second derivative of position with respect to time,

$$a = \frac{d^2x}{dt^2} \tag{1.74}$$

We shall encounter this equation in Section 1.9 again. We also shall find that the second derivatives of trigonometric functions are quite important:

$$\frac{d^2\sin(ax)}{dx^2} = \frac{d}{dx}\{a\ \cos(ax)\} = -a^2\ \sin(ax) \tag{1.75}$$

In other words, the second derivative of the sine function is just the negative sine function, multiplied by a constant. Notice that the derivative of a constant is zero, according to Eq. 1.70. Thus, the derivative of the function $f(x) = 2x^2 + 3x - 4$ (see Figure 1.5a) is

$$\frac{df(x)}{dx} = 4x + 3 \tag{1.76}$$

One of the important features of differential calculus is the fact that the derivative of a function easily lets us determine where maxima or minima of functions occur. Take the derivative shown in Eq. 1.76 as an example. At the minimum of the original function $f(x) = 2x^2 + 3x - 4$, its slope will be zero. Thus, we set

$$\frac{df(x)}{dx} = 4x + 3 = 0 \tag{1.77}$$

and obtain $x = -0.75$. Inspection of Figure 1.5a reveals that the minimum of the function $f(x) = 2x^2 + 3x - 4$, indeed, occurs at this abscissa value.

When taking the derivatives of products or quotients of functions, special rules (the product and quotient rules) of differentiation apply. Similarly, when the function to be differentiated involves nested functions, the chain rule of differentiation applies. Since these cases do not arise in the context of this book, these rules of differentiation are not discussed any further.

Integration is the inverse operation to differentiation, just like division is the inverse of multiplication, or taking the logarithm is the inverse to exponentiation. Since differentiation of a function f(x) was written as $\frac{df(x)}{dx}$, we define the inverse function as $\int f(x)dx$. This is called the indefinite integral, and, since it is the inverse of differentiation, we can write

for $f(x) = 1$, the integral is $\int 1\,dx = x$ and
for $f(x) = x$, the integral is $\int x\,dx = x^2/2$ (take these two integrals with a grain of salt, for the moment)

You can convince yourself that the derivative of the function $x^2/2$ is, indeed, x and demonstrate hereby that differentiation and integration are inverse functions.

Now to the grain of salt. You can easily convince yourself that the functions $\frac{1}{2}x^2$, $\frac{1}{2}x^2 + 2$ and $\frac{1}{2}x^2 + a$ all have the same derivative, x, since the constants in the functions disappear upon differentiation. Consequently, integration of the function $f(x) = x$ (i.e. performing the reverse of differentiation) cannot determine which of the three functions $\frac{1}{2}x^2$, $\frac{1}{2}x^2 + 2$, and $\frac{1}{2}x^2 + a$ was the original function. Therefore, we write the integral as

$$\int x dx = \frac{1}{2}x^2 + C \tag{1.78}$$

where C is a constant that can be 0, 2, or "a" in the examples given above. Therefore, we call the integral in Eq. 1.78 as the indefinite integral. The general rule for simple integration is

$$\int x^n\,dx = \frac{x^{n+1}}{n+1} + C \tag{1.79}$$

$$\int \frac{1}{x} dx = \ln x + C \tag{1.80}$$

$$\int e^x dx = e^x + C \tag{1.81}$$

$$\int \sin(x)\,dx = -\cos(x) + C \tag{1.82}$$

$$\int \cos(x)\,dx = \sin(x) + C \tag{1.83}$$

The ambiguity in the indefinite integral may be avoided by the use of the definite integral which may be interpreted as the area under the integrand f(x), delimited within the interval [a, b]:

$$\int_a^b f(x)dx = [F(x)]_a^b = F(b) - F(a) \tag{1.84}$$

Here, F(x) is the anti-derivative, or the inverse derivative of f(x), as defined in Eqs. 1.80 through Eq. 1.83, evaluated at the values "a" and "b". The area under the curve $f(x) = x^2$ shown in Figure 1.11 in the interval from 1 to 3 would be

$$\int_1^3 x^2 dx = \left[\frac{1}{3}\,x^3\right]_1^3 = \frac{1}{3}27 - \frac{1}{3} = 8\frac{2}{3} \tag{1.85}$$

where the super- and subscripts at the square bracket denote that F(x) has to be evaluated for the values "3" and "1."

1.9 Differential Equations

We encountered a simple differential equation in Chapter 13, when we found that the rate of a first-order reaction, expressed as the change in the concentration of A, $-\frac{d[A]}{dt}$, is proportional to the momentary concentration of A:

$$-\frac{d[A]}{dt} = k\,[A] \qquad (13.20)$$

which can be rewritten as

$$\frac{d[A]}{[A]} = -k\,dt$$

Taking the definite integral on both sides between time zero and a later time "t", with the condition that the concentration of A at t=0 was $[A]_o$ gives

$$\int_{t=0}^{t=t'} \frac{d[A]}{[A]} = -k\int_{t=0}^{t=t'} dt \qquad (1.86)$$

$$\ln\frac{[A]_{t'}}{[A]_0} = -k\,(t') \quad \text{or} \qquad (1.87)$$

$$\ln\frac{[A]_0}{[A]_{t'}} = k\,(t') \qquad (13.22)$$

This is one of the easiest differential equations that could be solved by just taking the definite integral on both sides of the equation. A slightly more complicated differential equation was encountered in Chapter 15, during the discussion of the vibration of a diatomic molecule. There, we discussed that the restoring force for the elongation of the bond (spring) between two masses is

$$F = k\,x \qquad (15.33)$$

With Newton's second law of motion, which states that force equals mass times acceleration, we may write this force as

$$F = m_R\,\frac{d^2x}{dt^2} \qquad (1.88)$$

where m_R is the reduced mass of the system defined in Eq. 15.35. Thus, we may write the equation of motion for a diatomic molecule as

$$\frac{d^2x}{dt^2} + \frac{k}{m_R}\,x = 0 \qquad (1.89)$$

Here, we need a solution of the form x(t) such that the second derivative of this function, $\frac{d^2x(t)}{dt^2}$ is equal to this function, multiplied by a constant. We have encountered functions that fulfill this condition before:

$$\frac{d^2\sin(ax)}{dx^2} = -a^2\,\sin(ax) \qquad (1.75)$$

Similarly, the cosine or exponential functions could be used as a trial function. We use

$$x(t) = A\,\sin(\omega t) \qquad (1.90)$$

as a trial function where ω is the angular frequency, $\omega = 2\pi\nu$ and A is an amplitude factor. Then

$$\frac{d^2x(t)}{dt^2} = -A\,\omega^2\,\sin(\omega t) \qquad (1.91)$$

Substituting this result back into Eq. 1.89 yields

$$-A\,\omega^2\sin(\omega t) + \frac{k}{m_R}A\,\sin(\omega t) = 0 \qquad (1.92)$$

from which we obtain (by cancelling A sin(ωt) on both sides of the equation)

$$\omega^2 = \frac{k}{m_R} \quad \text{or} \quad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{m_R}} \qquad (15.34)$$

(neglecting the negative root in the quadratic equation above).

1.10 Complex Numbers

Complex numbers are an extension of real numbers that consist of a real part and an imaginary part that contains the imaginary unit i, defined as $i = \sqrt{-1}$. Complex numbers are necessary to solve equations such as $x^2 = -9$, which has no solution in real number space but has solutions in complex number space, $x_{\pm} = \pm(3i)$. Complex numbers generally are represented as

$$z = a + b\,i \tag{1.93}$$

where "a" is the real part and "b i" the imaginary part. They are represented graphically in an x–y plane where x-axis represents the real part and y-axis the imaginary part.

In the context of the discussions in this book, complex numbers were encountered only once, in the discussion of the wave functions of p-orbitals (Eqs. 15.24 and 15.25) that contain an expression $e^{\pm i\varphi}$. At this point, it is important to realize that the functions $e^{\pm i\varphi}$ are not an exponential growth or decay function that were described by $e^{\pm x}$ (see Figure 1.7), but represent periodic functions in complex space. This was indicated before by Euler's formula,

$$e^{i\varphi} = \cos\varphi + \,i\sin\varphi \tag{15.26}$$

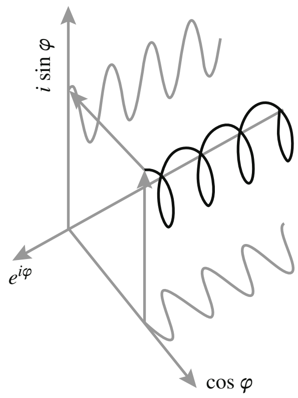

Figure 1.12 Visualization of the function $e^{i\varphi}$ as a periodical function in complex space. *Source:* Adapted from https://en.wikipedia.org/wiki/Euler%27s_formula.

which depicts a helical path for $e^{i\varphi}$ when plotted in a complex representation: $\cos\varphi$ being associated with the real, and $i\sin\varphi$ with the imaginary axis. A graphical depiction of this function is shown in Figure 1.12, which is adapted from https://en.wikipedia.org/wiki/Euler%27s_formula under "Visualization of Euler's formula as a helix in three-dimensional space." Although the concept of complex numbers may seem somewhat absurd at first, they appear frequently in physics, engineering, signal processing and mathematics.