1 Numbers, variables, and units

1.1 Concepts

Chemistry, in common with the other physical sciences, comprises

(i) **experiment**: the observation of physical phenomena and the measurement of physical quantities, and
(ii) **theory**: the interpretation of the results of experiment, the correlation of one set of measurements with other sets of measurements, the discovery and application of rules to rationalize and interpret these correlations.

Both experiment and theory involve the manipulation of numbers and of the symbols that are used to represent numbers and physical quantities. Equations containing these symbols provide relations amongst physical quantities. Examples of such equations are

1. the equation of state of the ideal gas

$$pV = nRT \tag{1.1}$$

2. Bragg's Law in the theory of crystal structure

$$n\lambda = 2d\sin\theta \tag{1.2}$$

3. the Arrhenius equation for the temperature dependence of rate of reaction

$$k = Ae^{-E_{\mathrm{a}}/RT} \tag{1.3}$$

4. the Nernst equation for the emf of an electrochemical cell

$$E = E^{\ominus} - \frac{RT}{nF}\ln Q \tag{1.4}$$

When an equation involves physical quantities, the expressions on the two sides of the equal sign[1] must be of the same kind as well as the same magnitude.

[1] The sign for equality was introduced by Robert Recorde (*c.* 1510–1558) in his *The whetstone of witte* (London, 1557); 'I will sette as I doe often in woorke use, a paire of paralleles, or Gemowe (twin) lines of one lengthe, thus: =, bicause noe.2. thynges can be moare equalle.'

EXAMPLE 1.1 The equation of state of the ideal gas, (1.1), can be written as an equation for the volume,

$$V = \frac{nRT}{p}$$

in which the physical quantities on the right of the equal sign are the pressure p of the gas, the temperature T, the amount of substance n, and the molar gas constant $R = 8.31447\ \text{J K}^{-1}\ \text{mol}^{-1}$.

We suppose that we have one tenth of a mole of gas, $n = 0.1$ mol, at temperature $T = 298$ K and pressure $p = 10^5$ Pa. Then

$$\begin{aligned} V = \frac{nRT}{p} &= \frac{0.1\ \text{mol} \times 8.31447\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}}{10^5\ \text{Pa}} \\ &= \left(\frac{0.1 \times 8.31447 \times 298}{10^5}\right) \times \left(\frac{\text{mol J K}^{-1}\ \text{mol}^{-1}\ \text{K}}{\text{Pa}}\right) \\ &= 2.478 \times 10^{-3}\ \text{m}^3 \end{aligned}$$

The quantities on the right side of the equation have been expressed in terms of SI units (see Section 1.8), and the combination of these units is the SI unit of volume, m^3 (see Example 1.17).

Example 1.1 demonstrates a number of concepts:

(i) Function. Given any particular set of values of the pressure p, temperature T, and amount of substance n, equation (1.1) allows us to calculate the corresponding volume V. The value of V is determined by the values of p, T, and n; we say

V is a **function** of *p*, *T*, and *n*.

This statement is usually expressed in mathematics as

$$V = f(p, T, n)$$

and means that, for given values of p, T and n, the value of V is given by the value of a function $f(p, T, n)$. In the present case, the function is $f(p, T, n) = nRT/p$. A slightly different form, often used in the sciences, is

$$V = V(p, T, n)$$

which means that V is *some* function of p, T and n, which may or may not be known.

Algebraic functions are discussed in Chapter 2. Transcendental functions, including the trigonometric, exponential and logarithmic functions in equations (1.2) to (1.4), are discussed in Chapter 3.

(ii) Constant and variable. Equation (1.1) contains two types of quantity:

Constant: a quantity whose value is fixed for the present purposes. The quantity $R = 8.31447\text{ J K}^{-1}\text{ mol}^{-1}$ is a constant physical quantity.[2] A constant number is any particular number; for example, $a = 0.1$ and $\pi = 3.14159\ldots$

Variable: a quantity that can have any value of a given set of allowed values. The quantities p, T, and n are the variables of the function $f(p, T, n) = nRT/p$.

Two types of variable can be distinguished. An **independent variable** is one whose value does not depend on the value of any other variable. When equation (1.1) is written in the form $V = nRT/p$, it is implied that the independent variables are p, T, and n. The quantity V is then the **dependent variable** because its value depends on the values of the independent variables. We could have chosen the dependent variable to be T and the independent variables as p, V, and n; that is, $T = pV/nR$. In practice, the choice of independent variables is often one of mathematical convenience, but it may also be determined by the conditions of an experiment; it is sometimes easier to measure pressure p, temperature T, and amount of substance n, and to calculate V from them.

Numbers are discussed in Sections 1.2 to 1.4, and variables in Section 1.5. The algebra of numbers (arithmetic) is discussed in Section 1.6.

(iii) A physical quantity is always the product of two quantities, a number and a **unit**; for example $T = 298.15\text{ K}$ or $R = 8.31447\text{ J K}^{-1}\text{ mol}^{-1}$. In applications of mathematics in the sciences, numbers by themselves have no meaning unless the units of the physical quantities are specified. It is important to know what these units are, but the mathematics does not depend on them. Units are discussed in Section 1.8.

1.2 Real numbers

The concept of number, and of counting, is learnt very early in life, and nearly every measurement in the physical world involves numbers and counting in some way. The simplest numbers are the **natural numbers**, the 'whole numbers' or signless integers $1, 2, 3, \ldots$ It is easily verified that the addition or multiplication of two natural numbers always gives a natural number, whereas subtraction and division may not. For example $5 - 3 = 2$, but $5 - 6$ is not a natural number. A set of numbers for which the operation of *subtraction* is always valid is the set of **integers**, consisting of all positive and negative whole numbers, and zero:

$$\cdots \quad -3 \quad -2 \quad -1 \quad 0 \quad +1 \quad +2 \quad +3 \quad \cdots$$

The operations of addition and subtraction of both positive and negative integers are made possible by the rules

$$\begin{aligned} m + (-n) &= m - n \\ m - (-n) &= m + n \end{aligned} \tag{1.5}$$

[2] The values of the fundamental physical constants are under continual review. For the latest recommended values, see the NIST (National Institute of Standards and Technology) website at www.physics.nist.gov

so that, for example, the subtraction of a negative number is equivalent to the addition of the corresponding positive number. The operation of multiplication is made possible by the rules

$$\begin{aligned}(-m)\times(-n)&=+(m\times n)\\(-m)\times(+n)&=-(m\times n)\end{aligned}\tag{1.6}$$

Similarly for division. Note that $-m=(-1)\times m$.

EXAMPLES 1.2 **Addition and multiplication of negative numbers**

$$\begin{array}{ll}2+(-3)=2-3=-1 & 2-(-3)=2+3=5\\(-2)\times(-3)=2\times 3=6 & (2)\times(-3)=-2\times 3=-6\\(-6)\div(-3)=6\div 3=2 & 6\div(-3)=-6\div 3=-2\end{array}$$

› Exercises 1–7

In equations (1.5) and (1.6) the letters m and n are symbols used to represent any pair of integers; they are **integer variables**, whose values belong to the (infinite) set of integers.

Division of one integer by another does not always give an integer; for example $6\div 3=2$, but $6\div 4$ is not an integer. A set of numbers for which the operation of *division* is always valid is the set of **rational numbers**, consisting of all the numbers $m/n=m\div n$ where m and n are integers (m/n, read as 'm over n', is the more commonly used notation for 'm divided by n'). The definition excludes the case $n=0$ because division by zero is not defined (see Section 1.6), but integers are included because an integer m can be written as $m/1$. The rules for the combination of rational numbers (and of fractions in general) are

$$\frac{m}{n}+\frac{p}{q}=\frac{mq+np}{nq}\tag{1.7}$$

$$\frac{m}{n}\times\frac{p}{q}=\frac{mp}{nq}\tag{1.8}$$

$$\frac{m}{n}\div\frac{p}{q}=\frac{m}{n}\times\frac{q}{p}=\frac{mq}{np}\tag{1.9}$$

where, for example, mq means $m\times q$.

EXAMPLES 1.3 **Addition of fractions**

(1) Add $\frac{1}{2}$ and $\frac{1}{4}$.

The number **one half** is equal to **two quarters** and can be added to **one quarter** to give **three quarters**:

$$\frac{1}{2}+\frac{1}{4}=\frac{2}{4}+\frac{1}{4}=\frac{3}{4}$$

The value of a fraction like $1/2$ is unchanged if the numerator and the denominator are both multiplied by the same number:

$$\frac{1}{2}=\frac{1\times 2}{2\times 2}=\frac{2}{4}$$

and the general method of adding fractions is (a) find a common denominator for the fractions to be added, (b) express all the fractions in terms of this common denominator, (c) add.

(2) Add $\frac{2}{3}$ and $\frac{4}{5}$.

A common denominator is $3\times 5=15$. Then

$$\frac{2}{3}+\frac{4}{5}=\frac{2\times 5}{3\times 5}+\frac{3\times 4}{3\times 5}=\frac{10}{15}+\frac{12}{15}=\frac{10+12}{15}=\frac{22}{15}$$

(3) Add $\frac{1}{4}$ and $\frac{5}{6}$.

A common denominator is $4\times 6=24$, but the lowest (smallest) common denominator is 12:

$$\frac{1}{4}+\frac{5}{6}=\frac{3}{12}+\frac{10}{12}=\frac{13}{12}$$

› Exercises 8–13

EXAMPLE 1.4 Multiplication of fractions

$$\frac{2}{3}\times\frac{4}{5}=\frac{2\times 4}{3\times 5}=\frac{8}{15}$$

This can be interpreted as taking two thirds of $4/5$ (or four fifths of $2/3$).

› Exercises 14–17

EXAMPLE 1.5 Division of fractions

$$\frac{2}{3}\div\frac{4}{5}=\frac{2}{3}\times\frac{5}{4}=\frac{10}{12}$$

The number $10/12$ can be simplified by 'dividing top and bottom' by the common factor 2: $10/12=5/6$ (see Section 1.3).

› Exercises 18–21

Every rational number is the solution of a linear equation

$$mx=n \tag{1.10}$$

where m and n are integers; for example, $3x=2$ has solution $x=2/3$. Not all numbers are rational however. One solution of the quadratic equation

$$x^2=2$$

is $x=\sqrt{2}$, the positive square root of 2 (the other solution is $-\sqrt{2}$), and this number cannot be written as a rational number m/n; it is called an **irrational number**. Other irrational numbers are obtained as solutions of the more general quadratic equation

$$ax^2+bx+c=0$$

where a, b, and c are arbitrary integers, and of higher-order algebraic equations; for example, a solution of the cubic equation

$$x^3=2$$

is $x=\sqrt[3]{2}$, the cube root of 2. Irrational numbers like $\sqrt{2}$ and $\sqrt[3]{2}$ are called **surd**s.

The rational and irrational numbers obtained as solutions of **algebraic equations** of type

$$a_0+a_1x+a_2x^2+a_3x^3+\cdots+a_nx^n=0 \tag{1.11}$$

where a_0, a_1, …, a_n are integers, are called **algebraic numbers**; these numbers can be expressed exactly in terms of a finite number of rational numbers and surds. There exist also other numbers that are not algebraic; they are not obtained as solutions of any finite algebraic equation. These numbers are irrational numbers called **transcendental numbers**; 'they transcend the power of algebraic methods'

(Euler).[3] The best known and most important of these are the Euler number *e* and the Archimedean number π.[4] These are discussed in Section 1.4.

The rational and irrational numbers form the **continuum of numbers**; together they are called the **real numbers**.

1.3 Factorization, factors, and factorials

Factorization is the decomposition of a number (or other quantity) into a product of other numbers (quantities), or **factors**; for example

$$30 = 2 \times 3 \times 5$$

shows the decomposition of the natural number 30 into a product of **prime numbers**; that is, natural numbers that cannot be factorized further (the number 1 is not counted as a prime number). The **fundamental theorem of arithmetic** is that every natural number can be factorized as a product of prime numbers in only one way.[5]

EXAMPLES 1.6 Prime number factorization

(1) $4 = 2 \times 2 = 2^2$

(2) $12 = 2 \times 2 \times 3 = 2^2 \times 3$

(3) $315 = 3 \times 3 \times 5 \times 7 = 3^2 \times 5 \times 7$

(4) $5120 = 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 5 = 2^{10} \times 5$

› Exercises 22–25

Factorization and cancellation of **common factors** can be used for the simplification of fractions. For example, in

$$\frac{12}{42} = \frac{\cancel{6} \times 2}{\cancel{6} \times 7} = \frac{2}{7}$$

[3] Leonhard Euler (1707–1783). Born in Switzerland, he worked most of his life in St Petersburg and in Berlin. One of the world's most prolific mathematicians, he wrote 'voluminous papers and huge textbooks'. He contributed to nearly all branches of mathematics and its application to physical problems, including the calculus, differential equations, infinite series, complex functions, mechanics, and hydrodynamics, and his name is associated with many theorems and formulas. One of his important, if unspectacular, contributions was to mathematical notation. He introduced the symbol *e*, gave the trigonometric functions their modern definition, and by his use of the symbols sin, cos, *i*, and π made them universally accepted.

[4] The symbol π was first used by William Jones (1675–1749) in a textbook on mathematics, *Synopsis palmariorum matheseos* (A new introduction to the mathematics) in 1706. Euler's adoption of the symbol ensured its acceptance.

[5] A version of the fundamental theorem of arithmetic is given by Propositions 31 and 32 in Book VII of Euclid's *Stoichia* (Elements). Euclid was one of the first teachers at the Museum and Library of Alexandria founded by Ptolemy I in about 300 BC after he had gained control of Egypt when Alexander's empire broke up in 323 BC.

cancellation of the common factor 6 is equivalent to dividing both numerator and denominator by 6, and such an operation does not change the value of the fraction.

EXAMPLES 1.7 Simplification of fractions

(1) $\frac{4}{24}=\frac{2^2}{2^3\times 3}=\frac{\cancel{2}\times\cancel{2}}{\cancel{2}\times\cancel{2}\times 2\times 3}=\frac{1}{6}$

(2) $\frac{15}{25}=\frac{3\times\cancel{5}}{5^{\cancel{2}}}=\frac{3}{5}$

(3) $\frac{105}{1470}=\frac{\cancel{3}\times\cancel{5}\times\cancel{7}}{2\times\cancel{3}\times\cancel{5}\times 7^{\cancel{2}}}=\frac{1}{2\times 7}=\frac{1}{14}$

› Exercises 26–29

In general, the purpose of factorization is to express a quantity in terms of simpler quantities (see Section 2.3 for factorization of algebraic expressions).

Factorials

The **factorial** of n is the number whose factors are the first n natural numbers:

$$\begin{aligned} n! &= 1\times 2\times 3\times\cdots\times n \\ &= n\times(n-1)\times(n-2)\times\cdots\times 2\times 1 \end{aligned} \tag{1.12}$$

(read as ‘n factorial’). Consecutive factorials are related by the recurrence relation

$$(n+1)! = (n+1)\times n!$$

for example, $3!=3\times 2\times 1=6$ and $4!=4\times 3\times 2\times 1=4\times 3!=24$. In addition, the factorial of zero is defined as $0!=1$.

EXAMPLES 1.8 Factorials

(1) $1!=1\times 0!=1\times 1=1$

(2) $5!=5\times 4!=5\times 4\times 3!=5\times 4\times 3\times 2!=5\times 4\times 3\times 2=120$

(3) $\frac{5!}{3!}=\frac{5\times 4\times\cancel{3}!}{\cancel{3}!}=5\times 4=20$

(4) $\frac{7!}{3!4!}=\frac{7\times\cancel{6}\times 5\times\cancel{4}!}{\cancel{3}\times\cancel{2}\times\cancel{4}!}=7\times 5=35$

› Exercises 30–36

1.4 Decimal representation of numbers

These are the nine figures of the Indians

9 8 7 6 5 4 3 2 1

With these nine figures, and with this sign 0 which in Arabic is called zephirum, any number can be written, as will below be demonstrated.

(Fibonacci)[6]

In the decimal system of numbers, the ten digit symbols 0 to 9 (Hindu-Arabic numerals)[7] are used for zero and the first nine positive integers; the tenth positive integer is denoted by 10. A larger integer, such as 'three hundred and seventy-two' is expressed in the form

$$300 + 70 + 2 = 3 \times 10^2 + 7 \times 10 + 2$$

and is denoted by the symbol 372, in which the value of each digit is dependent on its position in the symbol for the number. The decimal system has **base** 10, and is the only system in common use.

Although rational numbers can always be expressed exactly as ratios of integers, this is not so for irrational numbers. For computational purposes, a number that is not an integer is conveniently expressed as a **decimal fraction**;[8] for example, $5/4 = 1.25$. The general form of the decimal fraction

$$\text{(integral part).(fractional part)}$$

consists of an integer to the left of the decimal point, the integral part of the number, and one or more digits to the right of the decimal point, the decimal or fractional part of the number. The value of each digit is determined by its position; for example

$$\begin{aligned} 234.567 &= 200 + 30 + 4 + \frac{5}{10} + \frac{6}{100} + \frac{7}{1000} \\ &= 2 \times 10^2 + 3 \times 10^1 + 4 \times 10^0 + 5 \times 10^{-1} + 6 \times 10^{-2} + 7 \times 10^{-3} \end{aligned}$$

[6] Leonardo of Pisa, also called Fibonacci (*c.* 1170–after 1240). The outstanding mathematician of the Latin Middle Ages. In his travels in Egypt, Syria, Greece, and Sicily, Fibonacci studied Greek and Arabic (Muslim) mathematical writings, and became familiar with the Arabic positional number system developed by the Hindu mathematicians of the Indus valley of NW India. Fibonacci's first book, the *Liber abaci*, or Book of the Abacus, (1202, revised 1228) circulated widely in manuscript, but was published only in 1857 in *Scritti di Leonardo Pisano*. The first chapter opens with the quotation given above in the text.

[7] One of the principal sources by which the Hindu-Arabic decimal position system was introduced into (Latin) Europe was Al-Khwarizmi's *Arithmetic*. Muhammad ibn Musa Al-Khwarizmi (Mohammed the son of Moses from Khorezm, modern Khiva in Uzbekistan) was active in the time of the Baghdad Caliph Al-Mamun (813–833), and was probably a member of his 'House of Wisdom' (Academy) at a time when Baghdad was the largest city in the world. Al-Khwarizmi's *Algebra* was widely used in Arabic and in Latin translation as a source on linear and quadratic equations. The word algorithm is derived from his name, and the word algebra comes from the title, *Liber algebrae et almucabala*, of Robert of Chester's Latin translation (*c.* 1140) of his work on equations.

[8] The use of decimal fractions was introduced into European mathematics by the Flemish mathematician and engineer Simon Stevin (1548–1620) in his *De Thiende* (The art of tenths) in 1585. Although decimal fractions were used by the Chinese several centuries earlier, and the Persian astronomer Al-Kashi used decimal and sexagesimal fractions in his *Key to Arithmetic* early in the fifteenth century, the common use of decimal fractions in European mathematics can be traced directly to Stevin, especially after John Napier modified the notation into the present one with the decimal point (or decimal comma as is used in much of continental Europe). It greatly simplified the operations of multiplication and division.

where $10^{-n} = 1/10^n$ and $10^0 = 1$ (see Section 1.6).

› Exercises 37–42

A number with a finite number of digits after (to the right of) the decimal point can always be written in the rational form m/n; for example $1.234 = 1234/1000$. The converse is not always true however. The number $1/3$ cannot be expressed exactly as a finite decimal fraction:

$$\frac{1}{3} = 0.333\ldots$$

the dots indicating that the fraction is to be extended indefinitely. If quoted to four decimal places, the number has lower and upper bounds 0.3333 and 0.3334:

$$0.3333 < \frac{1}{3} < 0.3334$$

where the symbol < means 'is less than'; other symbols of the same kind are ≤ for 'is less than or equal to', > for 'is greater than', and ≥ for 'is greater than or equal to'. Further examples of nonterminating decimal fractions are

$$\frac{1}{7} = 0.142857\,142857\ldots, \qquad \frac{1}{12} = 0.083333\,333333\ldots$$

In both cases a finite sequence of digits after the decimal point repeats itself indefinitely, either immediately after the decimal point, as the sequence 142857 in $1/7$, or after a finite number of leading digits, as 3 in $1/12$. This is a characteristic property of rational numbers.

EXAMPLE 1.9 Express $1/13$ as a decimal fraction. By long division,

```
      0.07692307...
   13)1.00
        91
         90
         78
        120
        117
           30
           26
            40
            39
            100
             ⋮
```

The rational number $1/13 = 0.076923\,076923\ldots$ is therefore a nonterminating decimal fraction with repeating sequence 076923 after the decimal point.

› Exercises 43–46

An irrational number cannot be represented exactly in terms of a finite number of digits, and the digits after the decimal point do not show a repeating sequence. The number $\sqrt{2}$ has approximate value to 16 significant figures,

$$\sqrt{2} = 1.414213\ 562373\ 095\ldots$$

and can, in principle, be computed to any desired accuracy by a numerical method such as the Newton–Raphson method discussed in Chapter 20.[9]

The Archimedean number π

The number π is defined as the ratio of the circumference of a circle to its diameter. It is a transcendental number,[10] and has been computed to many significant figures; it was quoted to 127 decimal places by Euler in 1748. Its value to 16 significant figures is

$$\pi = 3.14159\ 26535\ 89793\ldots$$

The value of π has been of practical importance for thousands of years. For example, an Egyptian manuscript dated about 1650 BC (the Rhind papyrus in the British Museum) contains a prescription for the calculation of the volume of a cylindrical granary from which the approximate value $256/81 \approx 3.160$ can be deduced. A method for generating accurate approximations was first used by Archimedes[11] who determined the bounds

$$\frac{223}{71} < \pi < \frac{22}{7}$$

and the upper bound has an error of only 2 parts in a thousand.

[9] A clay tablet (YBC 7289, Yale Babylonian Collection) dating from the Old Babylonian Period (*c.* 1800–1600 BC) has inscribed on it a square with its two diagonals and numbers that give $\sqrt{2}$ to three sexagesimal places: $\sqrt{2} = 1, 24, 51, 10 = 1 + 24/60 + 51/60^2 + 10/60^3 \approx 1.41421296$, correct to 6 significant decimal figures.

[10] The proof of the irrationality of π was first given in 1761 by Johann Heinrich Lambert (1728–1777), German physicist and mathematician. He is also known for his introduction of hyperbolic functions into trigonometry. The number π was proved to be transcendental by Carl Louis Ferdinand von Lindemann (1852–1939) in 1882 by a method similar to that used by Hermite for *e*.

[11] Archimedes (287–212 BC) was born in Syracuse in Sicily. He made contributions to mathematics, mechanics, and astronomy, and was a great mechanical inventor. His main contributions to mathematics and the mathematical sciences are his invention of methods for determining areas and volumes that anticipated the integral calculus and his discoveries of the first law of hydrostatics and of the law of levers.

The Euler number *e*

The number e is defined by the 'infinite series' (see Chapter 7)

$$e = 1 + \frac{1}{1!} + \frac{1}{2!} + \frac{1}{3!} + \frac{1}{4!} + \cdots$$
$$= 2.71828\ 18284\ 59045\ldots$$

The value of e can be computed from the series to any desired accuracy. The number was shown to be a transcendental number by Hermite in 1873.[12]

EXAMPLE 1.10 Show that the sum of the first 10 terms of the series gives an approximate value of e that is correct to at least 6 significant figures.

$$e = 1 + 1 + \frac{1}{2} + \frac{1}{6} + \frac{1}{24} + \frac{1}{120} + \frac{1}{720} + \frac{1}{5040} + \frac{1}{40320} + \frac{1}{362880} + \frac{1}{3628800} + \cdots$$
$$\approx 1 + 1 + 0.5 + 0.166667 + 0.041667 + 0.008333 + 0.001389 + 0.000198$$
$$+ 0.000025 + 0.000003 + 0.0000003$$
$$\approx 2.71828$$

The value is correct to the 6 figures quoted because every additional term in the series is at least ten times smaller than the preceding one.

Significant figures and rounding

In practice, arithmetic involving only integers gives exact answers (unless the numbers are too large to be written). More generally, a number in the decimal system is approximated either with some given number of decimal places or with a given number of significant figures, and the result of an arithmetic operation is also approximate. In the **fixed-point** representation, all numbers are given with a fixed number of decimal places; for example,

$$3.142, \quad 62.358, \quad 0.013, \quad 1.000$$

have 3 decimal places. In the **floating-point** representation, used more widely in the sciences, the numbers are given with a fixed number of 'significant figures', with zeros on the left of a number not counted. For example,

$$3210 = 0.3210 \times 10^4, \quad 003.210 = 0.3210 \times 10^1, \quad 0.003210 = 0.3210 \times 10^{-2}$$

all have 4 significant figures.

[12] Charles Hermite (1822–1901). French mathematician, professor at the Sorbonne, is known for his work in algebra and number theory. His work on the algebra of complex numbers ('Hermitian forms') became important in the formulation of quantum theory. The Hermite differential equation and the Hermite polynomials are important in the solution of the Schrödinger equation for the harmonic oscillator.

A number whose exact (decimal) representation involves more than a given number of digits is reduced most simply by **truncation**; that is, by removing or replacing by zeros all superfluous digits on the right. For example, to 4 decimal places or 5 significant figures, 3.14159 is truncated to 3.1415. Truncation is not recommended because it can lead to serious computational errors. A more sensible (accurate) approximation of π to five figures is 3.1416, obtained by **rounding up**. The most widely accepted rules for rounding are:

(i) If the first digit dropped is *greater than or equal to* 5, the preceding digit is increased by 1; the number is *rounded up*.
(ii) If the first digit dropped is *less than* 5, the preceding digit is left unchanged; the number is *rounded down*. For example, for 4, 3, 2, and 1 decimal places,

$$7.36284 \quad \text{is} \quad 7.3628, \quad 7.363, \quad 7.36, \quad 7.4$$

Errors arising from truncation and rounding are discussed in Section 20.2.

› Exercises 47–49

1.5 Variables

In the foregoing sections, symbols (letters) have been used to represent arbitrary numbers. A quantity that can take as its value any value chosen from a given set of values is called a **variable**. If $\{x_1, x_2, x_3, \ldots, x_n\}$ is a set of objects, not necessarily numbers, then a variable x can be defined in terms of this set such that x can have as its value any member of the set; the set forms the **domain** of the variable. In (real) number theory, the objects of the set are real numbers, and a **real variable** can have as its domain either the whole continuum of real numbers or a subset thereof. If the domain of the variable x is an interval a to b,

$$a \le x \le b$$

then x is a **continuous variable** in the interval, and can have any value in the continuous range of values a to b (including a and b). If the domain consists of a discrete set of values, for example the n numbers $x_1, x_2, x_3, \ldots, x_n$, then x is called a **discrete variable**. If the domain consists of integers, x is an **integer variable**. If the set consists of only one value then the variable is called a **constant variable**, or simply a **constant**.

In the physical sciences, variables are used to represent both numbers and physical quantities. In the ideal-gas example discussed in Section 1.1, the physical quantities p, V, n, and T are continuous variables whose numerical values can in principle be any positive real numbers. Discrete variables are normally involved whenever objects are counted as opposed to measured. Typically, an integer variable is used for the counting and the counted objects form a sample of some discrete set. In some cases however a physical quantity can have values, some of which belong to a discrete set and others to a continuous set. This is the case for the energy levels and the observed spectral frequencies of an atom or molecule.

EXAMPLE 1.11 The spectrum of the hydrogen atom

The energy levels of the hydrogen atom are of two types:

(i) Discrete (quantized) energy levels with (negative) energies given by the formula (in atomic units, see Section 1.8)

$$E_n = -\frac{1}{2n^2}, \quad n = 1, 2, 3, \ldots$$

The corresponding states of the atom are the 'bound states', in which the motion of the electron is confined to the vicinity of the nucleus. Transitions between the energy levels give rise to discrete lines in the spectrum of the atom.

(ii) Continuous energy levels, with all positive energies, $E > 0$. The corresponding states of the atom are those of a free (unbound) electron moving in the presence of the electrostatic field of the nuclear charge. Transitions between these energy levels and those of the bound states give rise to continuous ranges of spectral frequencies.

1.6 The algebra of real numbers

The importance of the concept of variable is that variables can be used to make statements about the properties of whole sets of numbers (or other objects), and it allows the formulation of a set of rules for the manipulation of numbers. The set of rules is called the **algebra**.

Let *a*, *b*, and *c* be variables whose values can be any real numbers. The basic rules for the combination of real numbers, the algebra of real numbers or the arithmetic, are

1. $a + b = b + a$ (commutative law of addition)
2. $ab = ba$ (commutative law of multiplication)
3. $a + (b + c) = (a + b) + c$ (associative law of addition)
4. $a(bc) = (ab)c$ (associative law of multiplication)
5. $a(b + c) = ab + ac$ (distributive law)

The operations of addition and multiplication and their inverses, subtraction and division, are called **arithmetic operations**. The symbols +, −, × and ÷ (or /) are called **arithmetic operators**. The result of adding two numbers, $a + b$, is called the **sum** of *a* and *b*; the result of multiplying two numbers, $ab = a \times b = a \cdot b$, is called the **product** of *a* and *b*.[13]

[13] In 1698 Leibniz wrote in a letter to Johann Bernoulli: 'I do not like × as a symbol for multiplication, as it easily confounded with x … often I simply relate two quantities by an interposed dot'. It is becoming accepted practice to place the 'dot' in the 'high position' to denote multiplication $(2 \cdot 5 = 2 \times 5)$ and in the 'low position', on the line, for the decimal point $(2.5 = 5/2)$. An alternative convention, still widely used, is to place the dot on the line for multiplication $(2.5 = 2 \times 5)$ and high for the decimal point $(2 \cdot 5 = 5/2)$.

EXAMPLES 1.12 **Examples of the rules of arithmetic**

rule	**examples**
1. $a+b=b+a$	$2+3=3+2=5$
2. $ab=ba$	$2\times 3=3\times 2=6$
3. $a+(b+c)=(a+b)+c$	$\begin{cases}2+(3+4)=2+7=9, \text{ and}\\(2+3)+4=5+4=9\end{cases}$
4. $a(bc)=(ab)c$	$\begin{cases}2\times(3\times 4)=2\times 12=24, \text{ and}\\(2\times 3)\times 4=6\times 4=24\end{cases}$
5. $a(b+c)=ab+ac$	$\begin{cases}2\times(3+4)=2\times 7=14, \text{ and}\\2\times(3+4)=(2\times 3)+(2\times 4)=6+8=14\end{cases}$
	$-2(3+4)=(-2\times 3)+(-2\times 4)=-6-8=-14$
	$-2(3-4)=-2\times 3-2\times(-4)=-6+8=2$
A corollary to rule **5** is	
$(a+b)(c+d)=a(c+d)+b(c+d)$	$(2+3)(4+5)=2(4+5)+3(4+5)=18+27=45$

Three rules define the properties of zero and unity:

6. $a+0=0+a=a$ (addition of zero)

7. $a\times 0=0\times a=0$ (multiplication by zero)

8. $a\times 1=1\times a=a$ (multiplication by unity)

We have already seen that subtraction of a number is the same as addition of its negative, and that division by a number is the same as multiplication by its inverse. However, division by zero is not defined; there is no number whose inverse is zero. For example, the number $1/a$, for positive values of a, becomes arbitrarily large as the value of a approaches zero; we say that $1/a$ **tends to infinity** as a tends to zero:

$$\frac{1}{a}\to\infty \quad \text{as} \quad a\to 0$$

Although 'infinity' is represented by the symbol ∞, it is not a number. If it were a number then, by the laws of algebra, the equations $1/0=\infty$ and $2/0=\infty$ would imply $1=2$.

The **modulus** of a real number a is defined as the positive square root of a^2; $|a|=+\sqrt{a^2}$ (read as 'mod a'). It is the 'magnitude' of the number, equal to $+a$ if a is positive, and equal to $-a$ if a is negative:

$$|a|=\begin{cases}+a & \text{if } a>0\\ -a & \text{if } a<0\end{cases} \tag{1.13}$$

For example, $|3|=3$ *and* $|-3|=3$.

The index rule

Numbers are often written in the form a^m, where a is called the **base** and m is the **index** or **exponent**; for example, $100 = 10^2$ with base 10 and exponent 2, and $16 = 2^4$ with base 2 and exponent 4. When m is a positive integer, a^m is the mth power of a; for $m = 3$,

$$a^3 = a \times a \times a, \quad (-a)^3 = (-a)\times(-a)\times(-a) = (-1)^3 \times a^3 = -a^3$$

Numbers are also defined with negative and non-integral exponent. In practice, the number a^m is read 'a to the power m' or 'a to the m', even when m is not a positive integer. The rule for the product of numbers in base–index form is

9. $a^m a^n = a^{m+n}$ (index rule)

For example,

$$a^3 a^2 = (a \times a \times a)\times(a \times a) = a \times a \times a \times a \times a = a^5 = a^{3+2}$$

Three auxiliary rules are

10. $a^m/a^n = a^{m-n}$ **11.** $(a^m)^n = (a^n)^m = a^{m\times n}$ **12.** $(ab)^m = a^m b^m$

Rule **10** defines numbers with zero and negative exponents. Thus, setting $m = n$,

$$a^n/a^n = a^{n-n} = a^0 = 1$$

and any number raised to power zero is unity; for example, $2^3/2^3 = 2^{3-3} = 2^0 = 1$ because $2^3/2^3 = 1$. Also, setting $m = 0$ in rule **10**,

$$a^0/a^n = 1/a^n = a^{-n}$$

so that the inverse of a^n is a^{-n}. In particular, $1/a = a^{-1}$.

EXAMPLES 1.13 **The index rule**

rule	examples
9. $a^m a^n = a^{m+n}$	(a) $2^3 \times 2^2 = 2^{3+2} = 2^5$
	(b) $3^6 \times 3^{-3} = 3^{6-3} = 3^3$
	(c) $2^{1/2} \times 2^{1/4} = 2^{1/2+1/4} = 2^{3/4}$
10. $a^m/a^n = a^{m-n}$	(d) $2^{3/4}/2^{1/4} = 2^{3/4-1/4} = 2^{1/2}$
	(e) $2^4/2^{-2} = 2^{4-(-2)} = 2^{4+2} = 2^6$
	(f) $3^4/3^4 = 3^{4-4} = 3^0 = 1$

11. $(a^m)^n = (a^n)^m = a^{m\times n}$

(g) $(2^2)^3 = (2^2)\times(2^2)\times(2^2) = 2^{2\times 3} = 2^6$

(h) $(2^{1/2})^2 = 2^{(1/2)\times 2} = 2^1 = 2$

(i) $(2^3)^{4/3} = (2^{4/3})^3 = 2^{3\times 4/3} = 2^4$

(j) $(2^{\sqrt{2}})^{\sqrt{2}} = 2^{\sqrt{2}\times\sqrt{2}} = 2^2 = 4$

12. $(ab)^m = a^m b^m$

(k) $(2\times 3)^2 = 2^2\times 3^2$

(l) $(-8)^{1/3} = (-1)^{1/3}\times 8^{1/3} = (-1)\times 2 = -2$

› Exercises 50–65

Example 1.13(h) shows that $2^{1/2}\times 2^{1/2} = 2$. It follows that $2^{1/2} = \sqrt{2}$, the square root of 2. In general, for positive integer *m*, $a^{1/m}$ is the *m*th root of *a*:

$$a^{1/m} = \sqrt[m]{a}$$

Thus, $2^{1/3}$ is a cube root of 2 because $(2^{1/3})^3 = 2^{(1/3)\times 3} = 2^1 = 2$. More generally, for rational exponent m/n, rule **11** gives

$$a^{m/n} = (a^m)^{1/n} = (a^{1/n})^m$$

or, equivalently,

$$a^{m/n} = \sqrt[n]{a^m} = (\sqrt[n]{a})^m$$

so that $a^{m/n}$ is both the *n*th root of the *m*th power of *a* and the *m*th power of the *n*th root. For example,

$$4^{3/2} = (4^3)^{1/2} = (4^{1/2})^3 = 8$$

Although the index rules have been demonstrated only for integral and rational indices, they apply to all numbers written in the base–index form. When the exponent *m* is a variable, a^m is called an exponential function (see Section 3.6 for real exponents and Chapter 8 for complex exponents). If $x = a^m$ then $m = \log_a x$ is the logarithm of *x* to base *a* (see Section 3.7).

Rules of precedence for arithmetic operations

An arithmetic expression such as

$$2 + 3\times 4$$

is ambiguous because its value depends on the order in which the arithmetic operations are applied. The expression can be interpreted in two ways:

$$(2+3)\times 4 = 5\times 4 = 20$$

with the parentheses indicating that the addition is to performed first, and

$$2+(3\times 4)=2+12=14$$

in which the multiplication is performed first. Ambiguities if this kind can always be resolved by the proper use of parentheses or other brackets. In case of more complicated expressions, containing nested brackets, the convention is to use parentheses as the innermost brackets, then square brackets, then braces (curly brackets). Evaluation then proceeds from the innermost bracketed expressions outwards; for example

$$\Big\{\Big[(2+3)\times 4\Big]+5\Big\}\times 6=\Big\{\Big[5\times 4\Big]+5\Big\}\times 6=\Big\{20+5\Big\}\times 6=25\times 6=150$$

As shown, increasing sizes of brackets can help to clarify the structure of the expression.

If in doubt use brackets.

Arithmetic expressions are generally evaluated by following the **rules of precedence** for arithmetic operations:

1. Brackets take precedence over arithmetic operators.
2. Exponentiation (taking powers) takes precedence over multiplication/division and addition/subtraction.
3. Multiplication and division take precedence over addition and subtraction.
4. Addition and subtraction are performed last.

EXAMPLES 1.14 **Rules of precedence for arithmetic operations**

(1) $\begin{cases} 2+3\times 4=2+(3\times 4)=2+12=14 & \text{(rule 3)} \\ \text{but } (2+3)\times 4=5\times 4=20 & \text{(rule 1)} \end{cases}$

(2) $\begin{cases} 2+3\times 4\times 5+6=2+(3\times 4\times 5)+6=2+60+6=68 & \text{(rule 3)} \\ \text{but } (2+3)\times 4\times(5+6)=5\times 4\times 30=600 & \text{(rule 1)} \end{cases}$

(3) $\begin{cases} 2+3^2=2+9=11 & \text{(rule 2)} \\ \text{but } (2+3)^2=5^2=25 & \text{(rule 1)} \end{cases}$

(4) $\begin{cases} 9+16^{1/2}=9+4=11 & \text{(rule 2)} \\ \text{but } (9+16)^{1/2}=(25)^{1/2}=5 & \text{(rule 1)} \end{cases}$

(5) $\begin{cases} 3\times 4^2=3\times(4^2)=3\times 16=48 & \text{(rule 2)} \\ \text{but } (3\times 4)^2=(12)^2=144 & \text{(rule 1)} \end{cases}$

(6) $\begin{cases} 2\times 6\div 3=(2\times 6)\div 3=12\div 3=4 \\ \text{and } 2\times 6\div 3=2\times(6\div 3)=2\times 2=4 \end{cases}$

What not to do: $(a+b)^n \neq a^n + b^n$, where $\neq$ means 'is not equal to'. Thus,

$$\text{in case (3): } (2+3)^2 \neq 2^2 + 3^2, \quad \text{in case (4): } (9+16)^{1/2} \neq 9^{1/2} + 16^{1/2}$$

› Exercises 66–77

1.7 Complex numbers

The solutions of algebraic equations are not always real numbers. For example, the solutions of the equation

$$x^2 = -1 \text{ are } x = \pm\sqrt{-1}$$

and these are not any of the numbers described in Section 1.2. They are incorporated into the system of numbers by defining the square root of -1 as a new number which is usually represented by the symbol i (sometimes j) with the property

$$i^2 = -1$$

The two square roots of an arbitrary negative real number $-x^2$ are then ix and $-ix$. For example,

$$\sqrt{-16} = \sqrt{(16)\times(-1)} = \sqrt{16}\times\sqrt{-1} = \pm 4i$$

Such numbers are called **imaginary** to distinguish them from real numbers. More generally, the number

$$z = x + iy$$

where x and y are real is called a **complex number**.

Complex numbers obey the same rules of algebra as real numbers; it is only necessary to remember to replace i^2 by -1 whenever it occurs. They are discussed in greater detail in Chapter 8.

EXAMPLE 1.15 Find the sum and product of the complex numbers $z_1 = 2 + 3i$ and $z_2 = 4 - 2i$.

Addition: $z_1 + z_2 = (2+3i) + (4-2i) = (2+4) + (3i-2i) = 6 + i$

Multiplication: $z_1 z_2 = (2+3i)(4-2i) = 2(4-2i) + 3i(4-2i)$

$$= 8 - 4i + 12i - 6i^2 = 8 + 8i + 6 = 14 + 8i$$

› Exercises 78, 79

1.8 Units

A physical quantity has two essential attributes, **magnitude** and **dimensions**. For example, the quantity '2 metres' has the dimensions of length and has magnitude equal to twice the magnitude of the metre. The metre is a constant physical quantity that defines the dimensions of the quantity and provides a scale for the specification of the magnitude of an arbitrary length; it is a **unit** of length. In general, a physical quantity is the product of a number and a unit. All physical quantities can be expressed in terms of the seven 'base' quantities whose names and symbols are listed in the first two columns of Table 1.1.

Table 1.1 Base physical quantities and SI units

Physical quantity	Symbol	Dimension	Name of SI unit	Symbol for SI unit
length	l	L	metre	m
mass	m	M	kilogram	kg
time	t	T	second	s
electric current	I	I	ampere	A
temperature	T	θ	kelvin	K
amount of substance	n	N	mole	mol
luminous intensity	I_v	J	candela	cd

The symbols in column 3 define the dimensions of the base physical quantities, and the dimensions of all other quantities (derived quantities) can be expressed in terms of them. For example, velocity (or more precisely, speed) is distance travelled in unit time, $l/t = lt^{-1}$, and has dimensions of length divided by time, LT^{-1}. The dimensions of a physical quantity are independent of the system of units used to describe its value. Every system of units must, however, conform with the dimensions.

A variety of systems of units are in use, many tailored to the needs of particular disciplines in the sciences. The recommended system for the physical sciences, and for chemistry in particular, is the International System of Units (SI)[14] which is based on the seven base units whose names and symbols are listed in columns 4 and 5 in Table 1.1. Every physical quantity has an SI unit determined by its dimensionality. The SI units of length and time are the metre, m, and the second, s; the corresponding SI unit of velocity is metre per second, $\mathrm{m/s} = \mathrm{m\ s^{-1}}$ (see Example 1.16(i)). In addition to the base units, a number of quantities that are particularly important in the physical sciences have been given SI names and symbols. Some of these are listed in Table 1.2.

We note that some physical quantities have no dimensions. This is the case for a quantity that is the ratio of two others with the same dimensions; examples are relative density, relative molar mass, and mole fraction. A less obvious example is (plane) angle which is defined as the ratio of two lengths (see Section 3.2).

[14] SI (Système International d'Unités) is the international standard for the construction and use of units (see the NIST website at www.physics.nist.gov). In addition, IUPAC (International Union of Pure and Applied Chemistry) provides the standard on chemical nomenclature and terminology, and on the measurement and evaluation of data (see www.iupac.org).

Table 1.2 SI derived units with special names and symbols

Physical quantity	Name	Symbol	Description	SI unit
frequency	hertz	Hz	events per unit time	s^{-1}
force	newton	N	mass × acceleration	$kg\ m\ s^{-2}$
pressure	pascal	Pa	force per unit area	$N\ m^{-2}$
energy, work, heat	joule	J	force × distance	N m
power	watt	W	work per unit time	$J\ s^{-1}$
electric charge	coulomb	C	current × time	A s
electric potential	volt	V	work per unit charge	$J\ C^{-1}$
electric capacitance	farad	F	charge per unit potential	$C\ V^{-1}$
electric resistance	ohm	Ω	potential per unit current	$V\ A^{-1}$
electric conductance	siemens	S	current per unit potential	Ω^{-1}
magnetic flux	weber	Wb	work per unit current	$J\ A^{-1}$
magnetic flux density	tesla	T	magnetic flux per unit area	$Wb\ m^{-2}$
inductance	henry	H	magnetic flux per unit current	$Wb\ A^{-1}$
plane angle	radian	rad	angle subtended by unit arc at centre of unit circle	1
solid angle	steradian	sr	solid angle subtended by unit surface at centre of unit sphere	1

› Exercises 80–90

EXAMPLES 1.16 Dimensions and units

(i) **Velocity** is rate of change of position with time, and has dimensions of length/time: LT^{-1}.

In general, the unit of a derived quantity is obtained by replacing each base quantity by its corresponding unit. In SI, the unit of velocity is meters per second, $m\ s^{-1}$. In a system in which, for example, the unit of length is the yard (yd) and the unit of time is the minute (min), the unit of velocity is yards per minute, $yd\ min^{-1}$. This 'non-SI' unit is expressed in terms of the SI unit by means of **conversion factors** defined within SI. Thus $1\ yd = 0.9144\ m$ (exactly), $1\ min = 60\ s$, and

$$1\ yd\ min^{-1} = (0.9144\ m) \times (60\ s)^{-1} = (0.9144/60)\ m\ s^{-1} = 0.01524\ m\ s^{-1}$$

(ii) **Acceleration** is rate of change of velocity with time, and has dimensions of velocity/time:

$$[\mathsf{LT}^{-1}] \times [\mathsf{T}^{-1}] = \mathsf{LT}^{-2}, \text{ with SI unit } m\ s^{-2}.$$

The standard acceleration of gravity is $g = 9.80665 \text{ m s}^{-2} = 980.665 \text{ Gal}$, where

$$\text{Gal} = 10^{-2} \text{ m s}^{-2} \text{ (cm s}^{-2}\text{) is called the } \textbf{galileo}.$$

(iii) **Force** has dimensions of mass × acceleration:

$$[\mathsf{M}] \times [\mathsf{LT}^{-2}] = \mathsf{MLT}^{-2}, \text{ with SI unit the } \textbf{newton}, \ \text{N} = \text{kg m s}^{-2}.$$

(iv) **Pressure** has dimensions of force per unit area:

$$[\mathsf{MLT}^{-2}]/[\mathsf{L}^2] = \mathsf{ML}^{-1}\mathsf{T}^{-2}, \text{ with SI unit the } \textbf{pascal}, \ \text{Pa} = \text{N m}^{-2} = \text{kg m}^{-1}\text{ s}^{-2}$$

Widely used alternative non-SI units for pressure are:

'standard pressure':	$\text{bar} = 10^5 \text{ Pa}$
atmosphere:	$\text{atm} = 101325 \text{ Pa}$
torr:	$\text{Torr} = (101325/760) \text{ Pa} \approx 133.322 \text{ Pa}$

(v) **Work, energy and heat** are quantities of the same kind, with the same dimensions and unit. Thus, work has dimensions of force × distance:

$$[\mathsf{MLT}^{-2}] \times [\mathsf{L}] = \mathsf{ML}^2\mathsf{T}^{-2}, \text{ with SI unit the } \textbf{joule}, \ \text{J} = \text{N m} = \text{kg m}^2\text{ s}^{-2}$$

and kinetic energy $\frac{1}{2}mv^2$ has dimensions of mass × (velocity)^2:

$$[\mathsf{M}] \times [\mathsf{LT}^{-1}]^2 = \mathsf{ML}^2\mathsf{T}^{-2}.$$

› Exercises 91–94

Dimensional analysis

The terms on both sides of an equation that contains physical quantities must have the same dimensions. Dimensional analysis is the name given to the checking of equations for dimensional consistency.

EXAMPLE 1.17 For the ideal-gas equation $pV = nRT$, equation (1.1), the dimensions of pV (using Tables 1.1 and 1.2) are those of work (or energy): $[\mathsf{ML}^{-1}\mathsf{T}^{-2}] \times [\mathsf{L}^3] = \mathsf{ML}^2\mathsf{T}^{-2}$. The corresponding expression in terms of SI units is

$$\text{Pa} \times \text{m}^3 = \text{N m}^{-2} \times \text{m}^3 = \text{N m} = \text{J}.$$

For nRT,

$$(\text{mol})(\text{J K}^{-1}\text{ mol}^{-1})(\text{K}) = \text{J}$$

as required. It follows that when equation (1.1) is written in the form $V = nRT/p$, as in Example 1.1, the dimensions of V are energy/pressure, with SI unit

$$\frac{\mathrm{J}}{\mathrm{Pa}} = \frac{\not{\mathrm{N}}\,\mathrm{m}}{\not{\mathrm{N}}\,\mathrm{m}^{-2}} = \mathrm{m}^3 \text{ for the volume.}$$

› Exercise 95

Large and small units

Decimal multiples of SI units have names formed from the names of the units and the prefixes listed in Table 1.3. For example, a picometre is $\mathrm{pm} = 10^{-12}$ m, a decimetre is $\mathrm{dm} = 10^{-1}$ m. These units of length are frequently used in chemistry; molecular bond lengths in picometres, and concentrations in moles per decimetre cube, $\mathrm{mol\ dm^{-3}} = 10^3\ \mathrm{mol\ m^{-3}}$.

Table 1.3 SI prefixes

Multiple	Prefix	Symbol	Multiple	Prefix	Symbol
10	deca	da	10^{-1}	deci	d
10^2	hecto	h	10^{-2}	centi	c
10^3	kilo	k	10^{-3}	milli	m
10^6	mega	M	10^{-6}	micro	μ
10^9	giga	G	10^{-9}	nano	n
10^{12}	tera	T	10^{-12}	pico	p
10^{15}	peta	P	10^{-15}	femto	f
10^{18}	exa	E	10^{-18}	atto	a
10^{21}	zetta	Z	10^{-21}	zepto	z
10^{24}	yotta	Y	10^{-24}	yocto	y

› Exercises 96–103

The quantities that are of interest in chemistry often have very different magnitudes from those of the SI units themselves, particularly when the properties of individual atoms and molecules are considered. For example, the mole is defined as the amount of substance that contains as many elementary entities (atoms or molecules) as there are atoms in 12 g (0.012 kg) of ^{12}C. This number is given by Avogadro's constant, $N_A \approx 6.02214 \times 10^{23}\ \mathrm{mol^{-1}}$. The mass of an atom of ^{12}C is therefore

$$m(^{12}\mathrm{C}) = 12/(6.02214 \times 10^{23})\ \mathrm{g} \approx 2 \times 10^{-26}\ \mathrm{kg}$$

or $m(^{12}\mathrm{C}) = 12$ u, where

$$\mathrm{u} = 1/(6.02214 \times 10^{23})\ \mathrm{g} \approx 1.66054 \times 10^{-27}\ \mathrm{kg}$$

is called the **unified atomic mass unit** (sometimes called a **Dalton**, with symbol Da).

EXAMPLES 1.18 Molecular properties: mass, length and moment of inertia

(i) **mass**. Atomic and molecular masses are often given as relative masses: A_r for an atom and M_r for a molecule, on a scale on which $A_r(^{12}C) = 12$. On this scale, $A_r(^1H) = 1.0078$ and $A_r(^{16}O) = 15.9948$. The corresponding relative molar mass of water is

$$M_r(^1H_2{}^{16}O) = 2 \times A_r(^1H) + A_r(^{16}O) = 18.0105,$$

the molar mass is

$$M(^1H_2{}^{16}O) = 18.0105 \text{ g mol}^{-1} = 0.01801 \text{ kg mol}^{-1},$$

and the mass of the individual molecule is

$$m(^1H_2{}^{16}O) = M_r(^1H_2{}^{16}O) \times \text{u} = 2.9907 \times 10^{-26} \text{ kg}$$

(ii) **length**. The bond length of the oxygen molecule is $R_e = 1.2075 \times 10^{-10}$ m, and molecular dimensions are usually quoted in appropriate units such as the picometre $\text{pm} = 10^{-12}$ m or the nanometre $\text{nm} = 10^{-9}$ m in spectroscopy, and the Ångström $\text{Å} = 10^{-10}$ m or the Bohr radius $a_0 = 0.529177 \times 10^{-10}$ m $= 0.529177$ Å in theoretical chemistry. Thus, for O_2, $R_e = 1.2075$ Å $= 120.75$ pm.

(iii) **reduced mass and moment of inertia**. The moment of inertia of a system of two masses, m_A and m_B, separated by distance R is $I = \mu R^2$, where μ is the reduced mass, given by

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}, \qquad \mu = \frac{m_A m_B}{m_A + m_B}$$

Relative atomic masses can be used to calculate the reduced mass of a diatomic molecule. Thus for CO, $A_r(^{12}C) = 12$ and $A_r(^{16}O) = 15.9948$, and these are the atomic masses in units of the unified atomic mass unit u. Then

$$\mu(^{12}C^{16}O) = \left(\frac{12 \times 15.9948}{27.9948}\right)\left(\frac{\text{u}^{\not 2}}{\not \text{u}}\right) = 6.8562 \text{ u}$$
$$= 6.8562 \times 1.66054 \times 10^{-27} \text{ kg} = 1.1385 \times 10^{-26} \text{ kg}$$

The bond length of CO is $112.81 \text{ pm} = 1.1281 \times 10^{-10}$ m, so that the moment of inertia of the molecule is

$$I = \mu R^2 = (1.1385 \times 10^{-26} \text{ kg}) \times (1.1281 \times 10^{-10} \text{ m})^2$$
$$= 1.4489 \times 10^{-46} \text{ kg m}^2$$

The reduced mass and moment of inertia are of importance in discussions of vibrational and rotational properties of molecules.

› Exercises 104, 105

EXAMPLES 1.19 Molecular properties: wavelength, frequency, and energy

The wavelength λ and frequency ν of electromagnetic radiation are related to the speed of light by

$$c = \lambda\nu \tag{1.14}$$

(see Example 3.7), where $c = 2.99792 \times 10^8\ \mathrm{m\ s^{-1}} \approx 3 \times 10^8\ \mathrm{m\ s^{-1}}$. The energy of a photon is related to the frequency of its associated wave via Planck's constant $h = 6.62608 \times 10^{-34}\ \mathrm{J\ s}$:

$$E = h\nu \tag{1.15}$$

In a spectroscopic observation of the transition between two states of an atom or molecule, the frequency of the radiation emitted or absorbed is given by $h\nu = |\Delta E|$, where $\Delta E = E_2 - E_1$ is the energy of transition between states with energies E_1 and E_2. Different spectroscopic techniques are used to study the properties of atoms and molecules in different regions of the electromagnetic spectrum, and different units are used to report the characteristics of the radiation in the different regions. The values of frequency and wavelength are usually recorded in multiples of the SI units of hertz $(\mathrm{Hz} = \mathrm{s^{-1}})$ and metre (m), respectively, but a variety of units is used for energy. For example, the wavelength of one of the pair of yellow D lines in the electronic spectrum of the sodium atom is $\lambda = 589.76\ \mathrm{nm} = 5.8976 \times 10^{-7}\ \mathrm{m}$. By equation (1.14), this corresponds to frequency

$$\nu = \frac{c}{\lambda} = \frac{2.99792\times10^{8}\ \mathrm{m\ s^{-1}}}{5.8975\times10^{-7}\ \mathrm{m}} = 5.0833\times10^{14}\ \mathrm{s^{-1}}$$

and by equation (1.15), the corresponding energy of transition is

$$\Delta E = h\nu = (6.62608 \times 10^{-34}\ \mathrm{J\ s}) \times (5.0833 \times 10^{14}\ \mathrm{s^{-1}}) = 3.368 \times 10^{-19}\ \mathrm{J}$$

Energies are often quoted in units of the electron volt, eV, or as molar energies in units of $\mathrm{kJ\ mol^{-1}}$. The value of eV is the product of the protonic charge e (see Table 1.4) and the SI unit of electric potential $\mathrm{V} = \mathrm{J\ C^{-1}}$ (Table 1.2): $\mathrm{eV} = 1.60218 \times 10^{-19}\ \mathrm{J}$. The corresponding molar energy is

$$\begin{aligned} \mathrm{eV} \times N_A &= (1.60218 \times 10^{-19}\ \mathrm{J}) \times (6.02214 \times 10^{23}\ \mathrm{mol^{-1}}) \\ &= 96.486\ \mathrm{kJ\ mol^{-1}} \end{aligned} \tag{1.16}$$

where N_A is Avogadro's constant. For the sodium example,

$$\Delta E = 3.368 \times 10^{-19}\ \mathrm{J} = 2.102\ \mathrm{eV} \equiv 202.8\ \mathrm{kJ\ mol^{-1}}$$

Very often, the characteristics of the radiation are given in terms of the **wavenumber**

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{\Delta E}{hc} \tag{1.17}$$

This has dimensions of inverse length and is normally reported in units of the reciprocal centimetre, cm^{-1}. For the sodium example, $\lambda = 5.8976 \times 10^{-5}$ cm and

$$\tilde{\nu} = \frac{1}{5.8976 \times 10^{-5}\ \text{cm}} = 16956\ \text{cm}^{-1}$$

The second line of the sodium doublet lies at 16973 cm^{-1}, and the fine structure splitting due to spin–orbit coupling in the atom is $17\ cm^{-1}$.

In summary, the characteristics of the radiation observed in spectroscopy can be reported in terms of frequency ν in Hz (s^{-1}), wavelength λ in (multiples of) m, energy ΔE in units of eV, molar energy in units of kJ mol^{-1}, and wavenumber $\tilde{\nu}$ in units of cm^{-1}. These quantities are related by equations (1.14) to (1.17). Conversion factors for energy are

$$1\ \text{eV} = 1.60218 \times 10^{-19}\ \text{J} \equiv 96.486\ \text{kJ mol}^{-1} \equiv 8065.5\ \text{cm}^{-1}$$

› Exercises 106

Approximate calculations

Powers of 10 are often used as a description of **order of magnitude**; for example, if a length A is two orders of magnitude larger than length B then it is about $10^2 = 100$ times larger. In some calculations that involve a wide range of orders of magnitude it can be helpful, as an aid to avoiding errors, to calculate the order of magnitude of the answer before embarking on the full detailed calculation. The simplest way of performing such an 'order of magnitude calculation' is to convert all physical quantities to base SI units and to approximate the magnitude of each by an appropriate power of ten, possibly multiplied by an integer. Such calculations are often surprisingly accurate.

EXAMPLE 1.20 Order of magnitude calculations

(i) For the calculation of volume in Example 1.1 (ignoring units),

$$V = \frac{nRT}{p} = \frac{0.1 \times 8.31447 \times 298}{10^5} = 2.478 \times 10^{-3}$$

Two estimates of the answer are

(a) $V \approx \dfrac{10^{-1} \times 10 \times 10^2}{10^5} = 10^{-3}$ (b) $V \approx \dfrac{10^{-1} \times 8 \times 300}{10^5} = 2.4 \times 10^{-3}$

(ii) For the calculation of the moment of inertia of CO in Example 1.18 (ignoring units), $\mu = 1.1385 \times 10^{-26} \approx 10^{-26}$ and $R = 1.1281 \times 10^{-10} \approx 10^{-10}$, and an order of magnitude estimate of the moment of inertia is $I = \mu R^2 \approx (10^{-26}) \times (10^{-10})^2 = 10^{-46}$ (accurate value 1.4489×10^{-46}).

› Exercise 107

Atomic units

The equations of motion in quantum mechanics are complicated by the presence of the physical quantities m_e, the rest mass of the electron, e, the charge on the proton, h, Planck's constant, and ε_0, the permittivity of a vacuum. For example, the Schrödinger equation for the motion of the electron about the stationary nucleus in the hydrogen atom is

$$-\frac{h^2}{8\pi^2 m_e}\nabla^2\psi - \frac{e^2}{4\pi\varepsilon_0 r}\psi = E\psi \tag{1.18}$$

The four experimentally determined quantities can be used as base units for the construction of **atomic units** for all physical quantities whose dimensions involve length, mass, time, and electric current (the first four entries in Table 1.1). Some of the atomic units are listed in Table 1.4. The atomic units of length and energy have been given names: the unit of length, a_0, is called the **bohr**, and is the most probable distance of the electron from the nucleus in the ground state of the hydrogen atom (the radius of the ground-state orbit in the 'old quantum theory' of Bohr). The unit of energy, E_h, is called the **hartree**, and is equal to twice the ionization energy of the hydrogen atom. Atomic units are widely used in quantum chemistry. The convention is to express each physical quantity in an expression in atomic units, and then to delete the unit from the expression; for example, for a distance r, the dimensionless quantity r/a_0 is replaced by r. If this is done to equation (1.18) the resulting dimensionless equation is

$$-\frac{1}{2}\nabla^2\psi - \frac{1}{r}\psi = E\psi \tag{1.19}$$

Table 1.4 Atomic units

Physical quantity	Atomic unit	Value in SI units
mass	m_e	9.10938×10^{-31} kg
charge	e	1.60218×10^{-19} C
angular momentum	$\hbar = h/2\pi$	1.05457×10^{-34} J s
length	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	5.29177×10^{-11} m
energy	$E_h = m_e e^4/16\pi^2\varepsilon_0^2\hbar^2$	4.35974×10^{-18} J
time	$\hbar/E_h$	2.41888×10^{-17} s
electric current	$eE_h/\hbar$	6.62362×10^{-3} A
electric potential	E_h/e	2.72114×10^{1} V
electric dipole moment	ea_0	8.47835×10^{-30} C m
electric field strength	E_h/ea_0	5.14221×10^{11} V m^{-1}
electric polarizability	$4\pi\varepsilon_0 a_0^3$	1.64878×10^{-41} F m^2
magnetic dipole moment	$e\hbar/m_e$	1.85480×10^{-23} J T^{-1}
magnetic flux density	$\hbar/ea_0^2$	2.35052×10^{5} T
magnetizability	$e^2a_0^2/m_e$	7.89104×10^{-29} J T^{-2}

In this form the equation is often referred to as the 'Schrödinger equation in atomic units'. The results of computations are then numbers that must be reinterpreted as physical quantities. For example, the quantity E in equation (1.18) is an energy. Solution of equation (1.19) gives the numbers $E=-1/2n^2$, for all positive integers n, and these numbers are then interpreted as the energies $E=-1/2n^2\,E_h$.

EXAMPLE 1.21 The atomic unit of energy

By Coulomb's law, the potential energy of interaction of charges q_1 and q_2 separated by distance r is

$$V=\frac{q_1q_2}{4\pi\varepsilon_0 r}$$

where $\varepsilon_0=8.85419\times10^{-12}\text{ F m}^{-1}$ is the permittivity of a vacuum. For charges $q_1=Z_1e$ and $q_2=Z_2e$ separated by distance $r=Ra_0$,

$$V=\left(\frac{Z_1Z_2}{R}\right)\left(\frac{e^2}{4\pi\varepsilon_0 a_0}\right)$$

(i) To show that the unit is the hartree unit E_h in Table 1.4, use $a_0=4\pi\varepsilon_0\hbar^2/m_e e^2$:

$$\frac{e^2}{4\pi\varepsilon_0 a_0}=\left(\frac{e^2}{4\pi\varepsilon_0}\right)\div\left(\frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}\right)=\left(\frac{e^2}{4\pi\varepsilon_0}\right)\times\left(\frac{m_e e^2}{4\pi\varepsilon_0\hbar^2}\right)=\frac{m_e e^4}{16\pi^2\varepsilon_0^2\hbar^2}=E_h$$

(ii) To calculate the value of E_h in SI units, use the values of e and a_0 given in Table 1.4. Then

$$\frac{e^2}{4\pi\varepsilon_0 a_0}=\left(\frac{1.60218^2}{4\times3.14159\times8.85419\times5.29177}\right)\times\left(\frac{10^{-19}\times10^{-19}}{10^{-12}\times10^{-11}}\right)\times\left(\frac{\text{C}^2}{\text{F m}^{-1}\text{ m}}\right)$$

$$=(4.35975\times10^{-3})\times(10^{-15})\times(\text{C}^2\text{ F}^{-1})$$

From the definitions of the coulomb C and farad F in Table 1.2, $\text{F}=\text{C}^2\text{ J}^{-1}$ so that $\text{C}^2\text{ F}^{-1}=\text{J}$. Therefore

$$\frac{e^2}{4\pi\varepsilon_0 a_0}=4.35975\times10^{-18}\text{ J}=E_h$$

› Exercise 108

1.9 Exercises

Section 1.2

Calculate and express each result in its simplest form:

1. $3+(-4)$ **2.** $3-(-4)$ **3.** $(-3)-(-4)$ **4.** $(-3)\times(-4)$ **5.** $3\times(-4)$

6. $8\div(-4)$ **7.** $(-8)\div(-4)$ **8.** $\frac{1}{4}+\frac{1}{8}$ **9.** $\frac{3}{4}-\frac{5}{7}$ **10.** $\frac{2}{9}-\frac{5}{6}$

11. $\frac{1}{14}+\frac{2}{21}$ **12.** $\frac{1}{18}-\frac{2}{27}$ **13.** $\frac{11}{12}+\frac{3}{16}$ **14.** $\frac{1}{2}\times\frac{3}{4}$ **15.** $2\times\frac{3}{4}$

16. $\frac{2}{3}\times\frac{5}{6}$ **17.** $\left(-\frac{2}{3}\right)\times\left(-\frac{3}{4}\right)$ **18.** $\frac{3}{4}\div\frac{4}{5}$ **19.** $\frac{2}{3}\div\frac{5}{3}$ **20.** $\frac{2}{15}\div\frac{4}{5}$

21. $\frac{1}{3}\div\frac{1}{9}$

Section 1.3

Factorize in prime numbers:

22. 6 **23.** 80 **24.** 256 **25.** 810

Simplify by factorization and cancellation:

26. $\frac{3}{18}$ **27.** $\frac{21}{49}$ **28.** $\frac{63}{294}$ **29.** $\frac{768}{5120}$

Find the value of:

30. 2! **32.** 7! **33.** 10!

Evaluate by cancellation:

33. $\frac{3!}{2!}$ **34.** $\frac{6!}{3!}$ **35.** $\frac{5!}{3!2!}$ **36.** $\frac{10!}{7!3!}$

Section 1.4

Express as decimal fractions:

37. 10^{-2} **38.** 2×10^{-3} **39.** $2+3\times10^{-4}+5\times10^{-6}$ **40.** $\frac{3}{8}$ **41.** $\frac{1}{25}$ **42.** $\frac{5}{32}$

Find the repeating sequence of digits in the nonterminating decimal fraction representation of:

43. $\frac{1}{9}$ **44.** $\frac{1}{11}$ **45.** $\frac{1}{21}$ **46.** $\frac{1}{17}$

Use the rules of rounding to give each of the following to 8, 7, 6, 5, 4, 3, 2 and 1 significant figures:

47. $1/13 = 0.07692\,3076923$ **48.** $\sqrt{2} = 1.414213\,562373$ **49.** $\pi = 3.141592\,653589$

Section 1.6

Simplify if possible:

50. a^2a^3 **51.** a^3a^{-3} **52.** a^3a^{-4} **53.** a^3/a^2 **54.** a^5/a^{-4} **55.** $(a^3)^4$

56. $(a^2)^{-3}$ **57.** $(1/a^2)^{-4}$ **58.** $a^{1/2}a^{1/3}$ **59.** $(a^2)^{3/2}$ **60.** $(a^3b^6)^{2/3}$

61. $(a^3+b^3)^{1/3}$ **62.** $9^{1/2}$ **63.** $8^{2/3}$ **64.** $32^{3/5}$ **65.** $27^{-4/3}$

Evaluate:

66. $7-3\times2$ **67.** $7-(3\times2)$ **68.** $(7-3)\times2$ **69.** $7+3\times4-5$

70. $(7+3)\times4-5$ **71.** $4\div2\times7-2$ **72.** $4\div2+7\times2$ **73.** $8\times2\div4\div2$

74. $3+4^2$ **75.** $3+4\times5^2$ **76.** $25+144^{1/2}$ **77.** $(5^2+12^2)^{1/2}$

Section 1.7

Find the sum and product of the pairs of complex numbers:

78. $z_1 = 3 + 5i, z_2 = 4 - 7i$ **79.** $z_1 = 1 - 6i, z_2 = -5 - 4i$

Section 1.8

For each of the following dimensions give its SI unit in terms of base units (column 5 of Table 1.1) and, where possible, in terms of the derived units in Table 1.2; identify a physical quantity for each:

80. L^3 **81.** ML^{-3} **82.** NL^{-3} **83.** MLT^{-1} **84.** MLT^{-2} **85.** $\mathsf{ML}^2\mathsf{T}^{-2}$

86. $\mathsf{ML}^{-1}\mathsf{T}^{-2}$ **87.** IT **88.** $\mathsf{ML}^2\mathsf{I}^{-1}\mathsf{T}^{-3}$ **89.** $\mathsf{ML}^2\mathsf{T}^{-2}\mathsf{N}^{-1}$ **90.** $\mathsf{ML}^2\mathsf{T}^{-2}\mathsf{N}^{-1}\theta^{-1}$

91. Given that 1 mile (mi) is 1760 yd and 1 hour (h) is 60 min, express a speed of 60 miles per hour in **(i)** m s^{-1}, **(ii)** km h^{-1}.

92. **(i)** What is the unit of velocity in a system in which the unit of length is the inch (in = 2.54×10^{-2} m) and the unit of time is the hour (h)? **(ii)** Express this in terms of base SI units. **(iii)** A snail travels at speed 1.2 in min^{-1}. Express this in units yd h^{-1}, m s^{-1}, and km h^{-1}.

93. The non-SI unit of mass called the (international avoirdupois) pound has value 1 lb = 0.45359237 kg. The 'weight' of the mass in the presence of gravity is called the pound-force, lbf. Assuming that the acceleration of gravity is $g = 9.80665$ m s^{-2}, **(i)** express 1 lbf in SI units, **(ii)** express, in SI units, the pressure that is denoted (in some parts of the world) by psi = 1 lbf in^{-2}, **(iii)** calculate the work done (in SI units) in moving a body of mass 200 lb through distance 5 yd against the force of gravity.

94. The vapour pressure of water at 20°C is recorded as $p(H_2O, 20°C) = 17.5$ Torr. Express this in terms of **(i)** the base SI unit of pressure, **(ii)** bar, **(iii)** atm.

95. The root mean square speed of the particles of an ideal gas at temperature T is $c = (3RT/M)^{1/2}$, where $R = 8.31447$ J K^{-1} mol^{-1} and M is the molar mass. Confirm that c has dimensions of velocity.

Express in base SI units

96. dm^{-3} **97.** cm ms^{-2} **98.** g dm^{-3} **99.** mg pm µs^{-2} **100.** dg mm^{-1} ns^{-2}

101. GHz µm **102.** kN dm **103.** mmol dm^{-3}

104. Given relative atomic masses $A_r(^{14}N) = 14.0031$ and $A_r(^{1}H) = 1.0078$, calculate **(i)** the relative molar mass of ammonia, $M_r(^{14}N^{1}H_3)$, **(ii)** the molecular mass and **(iii)** the molar mass.

105. The bond length of HCl is $R_e = 1.2745 \times 10^{-10}$ m and the relative atomic masses are $A_r(^{35}Cl) = 34.9688$ and $A_r(^{1}H) = 1.0078$. **(i)** Express the bond length in (a) pm, (b) Å and (c) a_0. Calculate **(ii)** the reduced mass of the molecule and **(iii)** its moment of inertia.

106. The origin of the fundamental aborption band in the vibration–rotation spectrum of $^{1}H^{35}Cl$ lies at wavenumber $\tilde{\nu} = 2886$ cm^{-1}. Calculate the corresponding **(i)** frequency, **(ii)** wavelength, and **(iii)** energy in units of eV and kJ mol^{-1}.

107. In the kinetic theory of gases, the mean speed of the particles of gas at temperature T is $\bar{c} = (8RT/\pi M)^{1/2}$, where M is the molar mass. **(i)** Perform an order-of-magnitude calculation of $\bar{c}$ for N_2 at 298.15 K ($M = 28.01$ g mol^{-1}). **(ii)** Calculate $\bar{c}$ to 3 significant figures.

108. In the Bohr model of the ground state of the hydrogen atom, the electron moves round the nucleus in a circular orbit of radius $a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$, now called the Bohr (radius). Given $\varepsilon_0 = 8.85419 \times 10^{-12}$ F m^{-1}, use the units and values of m_e, e and $\hbar$ given in Table 1.4 to confirm **(i)** that a_0 is a length, and **(ii)** the value of a_0 in Table 1.4.