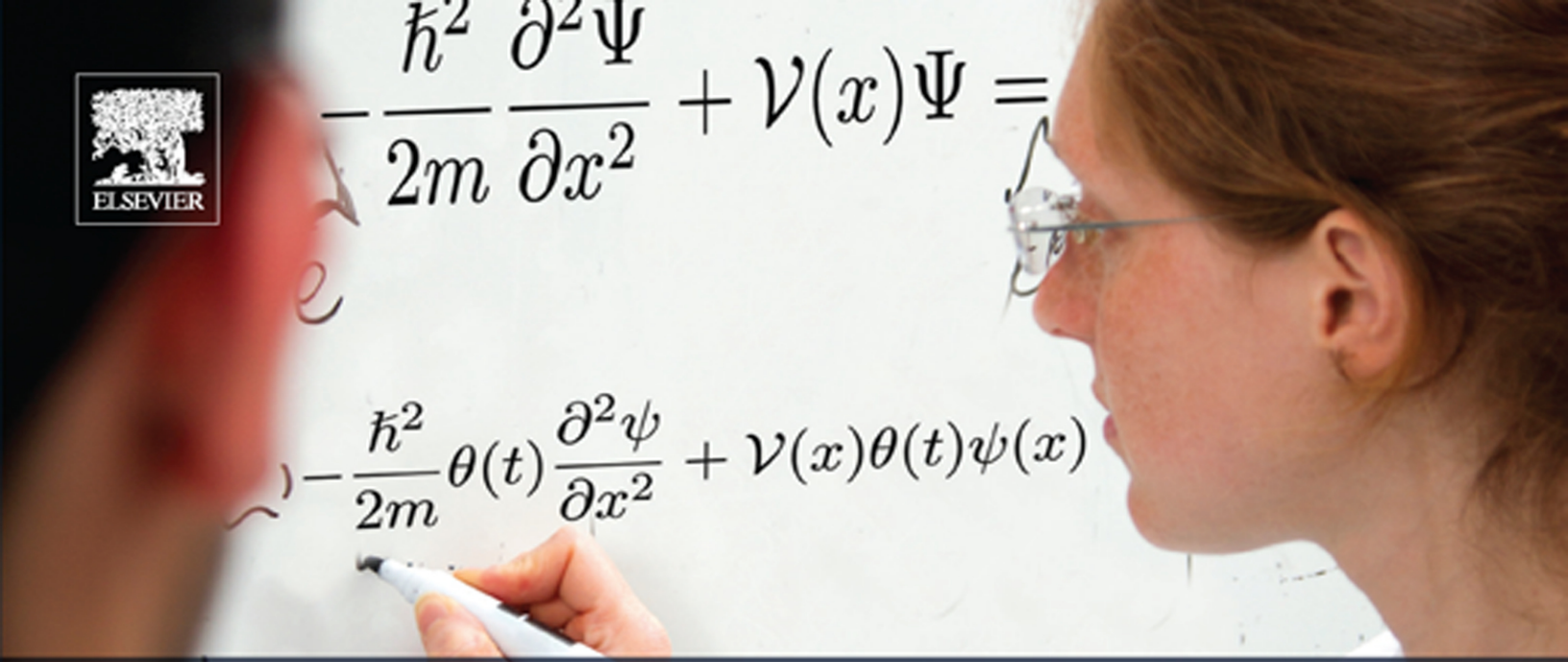

MATHEMATICS *for* PHYSICAL CHEMISTRY

FOURTH EDITION

ROBERT G. MORTIMER

Mathematics for Physical Chemistry

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Mathematics for Physical Chemistry

Fourth Edition

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Dedication

To my wife, Ann.

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Preface

This book provides a survey of the mathematics needed for chemistry courses at the undergraduate level. In four decades of teaching general chemistry and physical chemistry, I have found that some students have not been introduced to all of the mathematics needed in these courses and that most students need some practice in applying their mathematical knowledge to chemical problems. I once asked a student if he remembered some topic from elementary calculus. He didn't, but said, "They told me about it but didn't tell me that I would ever have to use it." The emphasis of this book is not on mathematical rigor, but on the use of the mathematics. I have tried to write all parts of this book so that they can be used for self-study by someone not familiar with the material, although any book such as this cannot be a substitute for the traditional mathematics courses. I have tried to write the book with a problem-solving approach.

Solved examples and exercises are interspersed throughout the chapters, and these form an important part of the presentations. As you study any topic in the book, you should follow the solution to each example and work each exercise as you come to it.

The book is constructed around a sequence of mathematical topics, with a gradual progression into more advanced material. Much of the material in the earlier chapters can be skipped if it is already sufficiently familiar to the reader. This edition is a revision of a third edition published by Elsevier/Academic Press in 2005. I have made those changes that seemed to improve the clarity and correctness of the presentations. Some of the examples, exercises, and problems have been modified, and some new ones have been added. A few of the chapters have been divided, and the sequence of chapters has been modified. I have continued to use a list of principal facts and ideas and a list of objectives at the beginning of each chapter but have removed the chapter summaries found in previous editions.

This book serves three functions:

1. a review of topics already studied and an introduction to new topics for those preparing for a course in physical chemistry,
2. a supplementary text to be used during a physical chemistry course, and
3. a reference book for advanced students and practicing chemists.

The Solutions Manual with solutions to nearly all of the exercises and problems can be found on the companion site at booksite.elsevier.com/9780124158092.

I am pleased to acknowledge the cooperation and help of Linda Versteeg-Buschman, Jill Cetel, Beth Campbell, and their collaborators at Elsevier.

It is also a pleasure to acknowledge the assistance of all those who helped with earlier editions of this book, and especially to thank my wife, Ann, for her patience, love, and forbearance.

Robert G. Mortimer

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Chapter 1

Problem Solving and Numerical Mathematics

Principal Facts and Ideas

- Problem solving is the principal tool for learning physical chemistry.
- Problem solving can be approached in a systematic way.
- Many problems involve numerical calculations involving measurable quantities.
- A measured quantity consists of a number and a unit of measurement.
- The SI units have been officially adopted by international organizations of physicists and chemists.
- Consistent units must be used in any calculation.
- The factor-label method can be used to convert from one unit of measurement to another.
- Reported values of all quantities should be rounded so that insignificant digits are not reported.

Objectives

After you have studied the chapter, you should be able to:

- analyze a problem and design a procedure for solving the problem;
- carry out the numerical procedures used in solving a simple problem;
- use numbers and units correctly to express measured quantities;
- understand the relationship of uncertainties in measurements to the use of significant digits;
- use consistent units, especially the SI units, in equations and formulas;
- use the factor-label method to convert from one unit of measurement to another.

1.1 PROBLEM SOLVING

Techniques of problem solving are applicable to many intellectual areas. There is a useful little book on problem solving by Polya,[1] and much of our discussion of problem solving is based on this book. Most physical chemistry problems are stated verbally, like the so-called "word problems" of elementary school. The information contained in the statement of the problem generally includes a statement of the physical system involved, some information about the state of the system, and a statement of the desired outcome. In many problems, the desired outcome is a numerical value of some variable that can be calculated. Following is a recipe for approaching such a problem:

1. Make sure that you know what is to be calculated.
2. Determine whether additional information not stated in the problem is needed.
3. Find such additional information, which might consist of formulas and values of variables.
4. Determine what procedures and calculations will get you to the desired result.
5. Carry out the necessary procedures and calculations.
6. Make sure that your result is reasonable.
7. Round off any insignificant digits.

1.2 NUMBERS AND MEASUREMENTS

Specification of a measurable quantity includes a number and a unit of measurement. For example, a length might

[1] G. Polya, *How to Solve it, a New Aspect of Mathematical Method*, Princeton University Press, Princeton, NJ, 1945. This book is out of print, but should be available in college and university libraries, and a few copies might still be available through Amazon.com.

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00001-X

be given as 12.00 inches (12.00 in) or 30.48 centimeters (30.48 cm), or 0.3048 meters (0.3048 m), and so on. Specification of the quantity is not complete until the unit of measurement is specified. For example, 30.48 cm is definitely not the same as 30.48 in. We discuss numbers now and units of measurement later.

There are several sets into which we can classify numbers. The first type consists of *real scalar numbers*. These are the numbers with which we most frequently deal, and they consist of a magnitude and a sign, which can be positive or negative. These numbers, together with the appropriate unit, can represent scalar variables, such as temperature or mass. Real scalar numbers can range from positive numbers of indefinitely large magnitude to negative numbers of indefinitely large magnitude. Among the real numbers are the *integers* $0, \pm 1, \pm 2, \pm 3$, and so on, which are part of the *rational numbers*. The nonnegative integers are sometimes called *whole numbers*. Other rational numbers are quotients of two integers, such as $\frac{2}{3}, \frac{7}{9}, \frac{37}{53}$, and so on, which we call *fractions*. Fractions can be represented in decimal form. For example, $\frac{1}{16}$ is the same as 0.0625. Some fractions cannot be represented exactly by a decimal number with a finite number of nonzero digits. For example, $\frac{1}{3}$ is represented by $0.333333\cdots$. The three dots (an *ellipsis*) that follow the given digits indicate that more nonzero digits follow. In this case, infinitely many digits are required for an exact representation. The decimal representation of a rational number either has a finite number of nonzero digits or contains a repeating pattern of digits. For instance, the decimal representation of $\frac{1}{11}$ is $0.09090909\cdots$ with infinitely many repetitions of the 09 pattern.

Exercise 1.1. Take a few fractions, such as $\frac{2}{3}, \frac{4}{9}$, or $\frac{3}{7}$, and represent them as decimal numbers, finding either all of the nonzero digits or the repeating pattern of digits.

The real numbers that are not rational numbers are called *irrational numbers*. *Algebraic irrational numbers* include square roots of rational numbers, cube roots of rational numbers, and so on, which are not themselves rational numbers. All of the rest of the irrational numbers are called *transcendental irrational numbers*. Two commonly encountered transcendental irrational numbers are the ratio of the circumference of a circle to its diameter, called π and given by $3.1415926535\cdots$,[2] and the *base of natural logarithms*, called e and given by $2.718281828\cdots$. The decimal representation of an irrational number does not have a finite number of nonzero digits, and does not contain a repeating pattern of digits.[3]

1.3 NUMERICAL MATHEMATICAL OPERATIONS

In solving a typical physical chemistry problem we are usually required to carry out numerical operations. This elementary discussion of these operations can be skipped without loss of continuity.

1.3.1 Binary Arithmetic Operations

These *binary mathematical operations* involving pairs of numbers are addition, subtraction, multiplication, and division. Some rules for operating on numbers with sign can be simply stated:

- The sum of two numbers of the same sign is obtained by adding the magnitudes and assigning the sign.
- The difference of two numbers is the same as the sum of the first number and the negative of the second.
- The product of two factors of the same sign is positive, and the product of two factors of different signs is negative.
- The quotient of two factors of the same sign is positive, and the quotient of two factors of different signs is negative.
- Multiplication is *commutative*, which means that[4]

$$\boxed{a \times b = b \times a}, \tag{1.1}$$

  where a and b represent two numbers.
- Multiplication is *associative*, which means that

$$\boxed{a \times (b \times c) = (a \times b) \times c}. \tag{1.2}$$

- Multiplication and addition are *distributive*, which means that

$$\boxed{a \times (b + c) = a \times b + a \times c}. \tag{1.3}$$

1.3.2 Additional Numerical Operations

In addition to the four binary arithmetic operations, there are some important mathematical operations that involve only one number (*unary operations*). The *magnitude*, or *absolute value*, of a scalar quantity is a nonnegative number that gives the size of the number irrespective of its sign. It is

[2] There is a mnemonic device with which you can remember the first 15 digits of pi. The number of letters in each word represents the digit: "Yes I need a drink, alcoholic of course, after the heavy sessions involving quantum mechanics."

[3] It has been said that early in the 20th century the legislature of the state of Indiana, in an effort to simplify things, passed a resolution that henceforth in that state, π should be exactly equal to 3.

[4] We enclose equations tbat you will likely use frequently in a box.

denoted by placing vertical bars before and after the symbol for the quantity. This operation means that the magnitude of x is given by

$$|x| = \begin{cases} x \text{ if } x \geqslant 0, \\ -x \text{ if } x < 0. \end{cases} \tag{1.4}$$

For example,

$$|4.5| = 4.5,$$
$$|-3| = 3.$$

The magnitude of a number is always nonnegative (positive or zero).

An important set of numerical operations involving a single number is the taking of *powers and roots*. If x represents some number that is multiplied by itself $n-1$ times so that there are n factors, we represent this by the symbol x^n, representing x to the nth power. For example,

$$x^2 = x \times x, \quad x^3 = x \times x \times x,$$
$$x^n = x \times x \times x \times \cdots \times x \quad (n \text{ factors}). \tag{1.5}$$

The number n in the expression x^n is called the *exponent* of x. An exponent that is a negative number indicates the reciprocal of the quantity with a positive exponent:

$$\boxed{x^{-1} = \tfrac{1}{x}, \quad x^{-3} = \tfrac{1}{x^3}}. \tag{1.6}$$

There are some important facts about exponents. The first is

$$\boxed{x^a x^b = x^{a+b}}, \tag{1.7}$$

where x, a, and b represent numbers. We call such an equation an *identity*, which means that it is correct for all values of the variables in the equation. The next identity is

$$\boxed{\left(x^a\right)^b = x^{ab}}. \tag{1.8}$$

Roots of real numbers are defined in an inverse way from powers. For example, the *square root* of x is denoted by $\sqrt{x}$ and is defined as the number that yields x when squared:

$$(\sqrt{x})^2 = x. \tag{1.9}$$

The *cube root* of x is denoted by $\sqrt[3]{x}$ and is defined as the number that when cubed (raised to the third power) yields x:

$$\left(\sqrt[3]{x}\right)^3 = x. \tag{1.10}$$

Fourth roots, fifth roots, and so on, are defined in similar ways. The operation of taking a root is the same as raising a number to a fractional exponent. For example,

$$\sqrt[3]{x} = x^{1/3}. \tag{1.11}$$

The order of taking a root and raising to a power can be reversed without changing the result

$$\left(\sqrt[3]{x}\right)^3 = (x^{1/3})^3 = x = (x^3)^{1/3} = \sqrt[3]{x^3}. \tag{1.12}$$

We say that these operations *commute* with each other.

There are two numbers that when squared will yield a given positive real number. For example, $2^2 = 4$ and $(-2)^2 = 4$. When the symbol $\sqrt{x}$ is used, the positive square root is always meant. To specify the negative square root of x, we write $-\sqrt{x}$. If we confine ourselves to real numbers, there is no square root, fourth root, sixth root, and so on, of a negative number. In a later chapter, we discuss imaginary numbers, which are defined to be square roots of negative quantities. Both positive and negative numbers can have real cube roots, fifth roots, and so on, since an odd number of negative factors yields a negative product.

1.4 UNITS OF MEASUREMENT

For many years science and commerce were hampered by the lack of accurately defined and universally accepted units of measurement. The history of units of measurement includes the definition of the yard as the distance from the nose of the King of England to the thumb of his outstretched arm and the definition of the meter as one ten-millionth of the distance from the North Pole to the equator on the line of longitude through Paris. Except for the unit of mass, these definitions have been replaced in terms of physical phenomena. The internationally accepted system of units of measurements is called the *Systéme International d'Unités*, abbreviated *SI*. This is an *MKS system*, which means that length is measured in meters, mass in kilograms, and time in seconds. Prior to 1960 chemists primarily used *cgs* units, based on centimeters, grams, and seconds.[5] In 1960 the international chemical community agreed to use SI units, which had been in use by physicists for some time. The seven base units given in the first part of Table 1.1. form the heart of the system. The second part of the table includes some derived units, which owe their definitions to the definitions of the seven base units.

Multiples and submultiples of SI units such as the millimeter and kilometer are commonly used. These multiples and submultiples are denoted by standard prefixes attached to the name of the unit, as listed in Table 1.2. The abbreviation for a multiple or submultiple is obtained by attaching the prefix abbreviation to the unit abbreviation, as in Gm (gigameter) or ns (nanosecond). Note that since the base unit of length is the kilogram, the table would imply the use of things such as the megakilogram. Double prefixes

[5] See "Policy for NBS Usage of SI Units," *J. Chem. Educ.* **48**, 569 (1971).

TABLE 1.1 SI Base Units (Units with Independent Definitions)

Physical quantity	Name of unit	Symbol	Definition
Length	meter	m	Length such that the speed of light is exactly 299,792,458 m s^{-1}
Mass	kilogram	kg	The mass of a platinum-iridium cylinder kept at the International Bureau of Weights and Measures in France
Time	second	s	The duration of 9,192,631,770 cycles of the radiation of a certain emission of the cesium atom
Electric current	Ampere	A	The magnitude of current which, when flowing in each of two long parallel wires 1 m apart in free space, results in a force of 2×10^7 N per meter of length
Temperature	Kelvin	K	Absolute zero is 0 K, the triple point of water is 273.16 K
Luminous intensity	candela	cd	The luminous intensity, in the perpendicular direction, of a surface of 1/600,000 m^2 of a black body at the temperature of freezing platinum and at a pressure of 101,325 N m^{-2}
Amount of substance	mole	mol	Amount of substance that contains as many elementary units as there are carbon atoms in exactly 0.012 kg of the carbon 12 (^{12}C) isotope

Other SI Units (Derived Units)

Physical quantity	Name of unit	Physical dimensions	Symbol	Definition
Force	Newton	kg m s^{-2}	N	1 N = 1 kg m s^{-2}
Energy	Joule	kg m^2 s^{-2}	J	1 J = 1 kg m^2 s^{-2}
Electrical charge	Coulomb	A s	C	1 C = 1 A s
Pressure	Pascal	N m^{-2}	Pa	1 Pa = 1 N m^{-2}
Magnetic field	Tesla	kg s^{-2} A^{-1}	T	1 T = 1 kg s^{-2} A^{-1} = 1 Wb m^{-2}
Luminous flux	Lumen	cd sr	lm	1 lm = 1 cd sr (sr = steradian)

TABLE 1.2 Prefixes for Multiple and Submultiple Units

Multiple	Prefix	Abbreviation	Multiple	Prefix	Abbreviation
10^{12}	tera-	T	10^{-3}	milli-	m
10^{9}	giga-	G	10^{-6}	micro-	μ
10^{6}	mega-	M	10^{-9}	nano-	n
10^{3}	kilo-	k	10^{-12}	pico-	p
1	—	—	10^{-15}	femto-	f
10^{-1}	deci-	d	10^{-18}	atto-	a
10^{-2}	centi-	c			

are not used. We use gigagram instead of megakilogram. The use of the prefixes for 10^{-1} and 10^{-2} is discouraged, but centimeters will probably not be abandoned for many years to come.[6]

Some non-SI units continue to be used, such as the *atmosphere* (atm), which is a unit of pressure defined to equal exactly 101,325 N m^{-2} (101,325 Pa), the *bar* (bar), defined to equal exactly 100,000 N m^{-2} (100,000 Pa), the *torr* (Torr), defined such that exactly 760 Torr equals exactly 1 atm, and the *liter* (l), which is a unit of volume exactly equal to 0.001 m^3. The *Celsius temperature scale* is defined such that the degree Celsius (°C) is the same size as the kelvin and such that 0 °C is equivalent to 273.15 K. The freezing point of water is 0.00 °C and the boiling point of water is 100.00 °C if the atmospheric pressure is 1.000 atm.

[6] There is a possibly apocryphal story about Robert A. Millikan, a Nobel-prize-winning physicist who was not noted for false modesty. A rival is supposed to have told Millikan that he had defined a new unit for the quantitative measure of conceit and had named the new unit the kan. However, 1 kan was an exceedingly large amount of conceit, so that for most purposes the practical unit was to be the millikan.

In the United States of America, English units of measurement are still in common use. The *inch* (in.) has been redefined to equal exactly 0.0254 m. The *foot* (ft) is exactly 12 in. and the mile (mi) is exactly 5280 ft. The *pound* (lb) is a unit of mass equal to 0.4536 kg (not an exact definition; good to four significant digits). There is also a system of units in which the pound is a unit of force and the corresponding unit of mass is called the slug. The Fahrenheit temperature scale is defined such that the freezing point of water is 32.00 °F and the boiling point of water is 212.00 °F.

A measured quantity is not completely specified until its units are given. If a is a length equal to 10.345 m, one must write

$$a = 10.345 \text{ m}, \tag{1.13}$$

not just

$$a = 10.345 \quad \text{(not correct)}. \tag{1.14}$$

It is permissible to write

$$a/\text{m} = 10.345, \tag{1.15}$$

which means that the length a divided by 1 m is 10.345, a dimensionless number. When constructing a table of values, it is convenient to label the columns or rows with such dimensionless quantities.

When you make numerical calculations, you should make certain that you use consistent units for all quantities. For example, you cannot correctly substitute a length in inches into a formula in which the other quantities are in SI units without converting. In setting up any calculation, it is a good idea to write the unit as well as the number, even for scratch calculations. This will help you avoid some kinds of mistakes by inspecting any equation and making sure that both sides are measured in the same units. In 1999 a US space vehicle optimistically named the *Mars Climate Orbiter* crashed into the surface of Mars instead of orbiting the planet. Engineers working on the project had used English units such as feet and pounds, whereas physicists had used metric units such as meters and kilograms. A failure to convert units properly cost US taxpayers several millions of dollars and the loss of a possibly useful mission. In another instance, when a Canadian airline switched from English units to metric units, a ground crew miscalculated the mass of fuel needed for a flight. The jet airplane ran out of fuel, but was able to glide to an unused military airfield and make a "deadstick" landing. Some people were having a picnic on the unused runway, but were able to get out of the way. There was even a movie made about the incident.

1.5 THE FACTOR-LABEL METHOD

This is an elementary method for the routine conversion of a quantity measured in one unit to the same quantity measured in another unit. The method consists of multiplying the quantity by a *conversion factor*, which is a fraction that is equal to unity in a physical sense, with the numerator and denominator equal to the same quantity expressed in different units. This does not change the quantity physically, but numerically expresses it in another unit. For example, to express 3.125 km in terms of meters, one writes

$$(3.125 \text{ km}) \left(\frac{1000 \text{ m}}{1 \text{ km}} \right) = 3125 \text{ m}. \tag{1.16}$$

You can check the units by considering a given unit to "cancel" if it occurs in both the numerator and denominator. Thus, both sides of this equation have units of meters, because the km on the top cancels the km on the bottom of the left-hand side. In applying the method, you should write out the factors explicitly, including the units. You should carefully check that the unwanted units cancel. Only then should you proceed to the numerical calculation. After the calculation you should think about whether the answer is approximately the correct size.

Example 1.1. Express the speed of light, 299,792,458 m s^{-1}, in miles per hour. Use the definition of the inch, 1 in. = 0.0254 m (exactly):

$$\begin{aligned} &\left(299{,}792{,}458 \text{ m s}^{-1}\right) \left(\frac{1 \text{ in.}}{0.0254 \text{ m}} \right) \left(\frac{1 \text{ ft}}{12 \text{ in.}} \right) \\ &\quad \left(\frac{1 \text{ mi}}{5280 \text{ ft}} \right) \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) \\ &\quad = 670{,}616{,}629 \text{ mi h}^{-1}. \end{aligned}$$

Exercise 1.2. Express the following in terms of SI base units. The electron volt (eV), a unit of energy, equals 1.6022×10^{-19} J:

(a) 13.6 eV.
(b) 24.17 mi.
(c) 55 mi h^{-1}.
(d) 7.53 nm ps^{-1}.

1.6 MEASUREMENTS, ACCURACY, AND SIGNIFICANT DIGITS

It is a good idea to communicate the probable accuracy of any measurement. For example, assume that you measured the length of a piece of glass tubing with a meter stick and that your measured value was 387.8 millimeters (387.8 mm). You decide on the basis of your experience that your experimental error was probably no greater than 0.6 mm. The best way to specify the length of the glass tubing is

$$\text{length} = 387.8 \text{ mm} \pm 0.6 \text{ mm}.$$

If you cannot include a statement of the probable error, you should at least avoid including digits that are probably wrongly stated. In this case, our estimated error is somewhat less than 1mm, so the correct number is probably closer to 388 mm than to either 387 mm or 389 mm. We can report the length as 388 mm and assert that the three digits given are *significant digits*, which means that we think they are correctly stated. It is a fairly common practice to consider a digit to be significant if it is uncertain by one unit. If we had reported the length as 387.8 mm, the last digit would not be a significant digit. That is, if we knew the exact length the digit eight after the decimal point is probably wrongly stated, since we can accurately say only that the correct length lies between 387.2 mm and 388.4 mm. You should not report insignificant digits in your final answer, but it is a good idea to carry at least one insignificant digit in your intermediate calculations to avoid accumulation of errors.

If you are given a number that you believe to be correctly stated, you can count the number of significant digits. If there are no zeros in the number, the number of significant digits is just the number of digits. If the number contains one or more zeros, any zero that occurs between nonzero digits does count as a significant digit. Any zeros that are present only to specify the location of a decimal point do not represent significant digits. For example, the number 0.0000345 contains three significant digits and the number 0.003045 contains four significant digits. The number 76,000 contains two significant digits. However, the number 0.000034500 contains five significant digits. The zeros at the left are needed to locate the decimal point, but the final two zeros are not needed to locate a decimal point, and therefore must have been included because the number is known with sufficient accuracy that these digits are significant. A problem arises when zeros that appear only to locate the decimal point are actually significant. For example, if a mass is known to be closer to 3500 grams (3500 g) than to 3499 g or to 3501 g, there are four significant digits. If one simply wrote 3500 g, persons with training in significant digits would assume that the zeros are not significant. Some people communicate the fact that there are four significant digits by writing 3500. The explicit decimal point communicates the fact that the zeros are significant digits. Others put a bar over any zeros that are significant, writing $35\bar{0}\bar{0}$ to indicate that there are four significant digits.

1.6.1 Scientific Notation

Communication difficulties involving significant zeros can be avoided by the use of *scientific notation*, in which a number is expressed as the product of two factors, one of which is a number lying between 1 and 10 and the other is 10 raised to some integer power. The mass mentioned above would be written as 3.500×10^3. There are four significant digits indicated, since the trailing zeros are not required to locate a decimal point. If the mass were known to only two significant digits, it would be written as 3.5×10^3 g. Scientific notation is also convenient for extremely small or extremely large numbers. For example, *Avogadro's constant*, the number of molecules or other formula units per mole, is easier to write as 6.0221367×10^{23} mol^{-1} than as 602,213,670,000,000,000,000,000 mol^{-1}, and the charge on an electron is easier to write and read as $1.60217733 \times 10^{-19}$ Coulomb ($1.6021733 \times 10^{-19}$ C) than as 0.000000000000000000016021733 C.

Example 1.2. Convert the following numbers to scientific notation:

(a) 0.005980

$$0.005980 = 5.980 \times 10^{-3}.$$

(b) 7,342,000

$$7{,}342{,}000 = 7.342 \times 10^{6}.$$

Exercise 1.3. Convert the following numbers to scientific notation:

(a) 0.00000234.
(b) 32.150.

1.6.2 Rounding

To remove insignificant digits, we must round a number. This process is straightforward in most cases. The calculated number is simply replaced by that number containing the proper number of digits that is closer to the calculated value than any other number containing this many digits. Thus, if there are three significant digits, 4.567 is rounded to 4.57, and 4.564 is rounded to 4.56. However, if your only insignificant digit is a 5, your indicated number is midway between two rounded numbers, and you must decide whether to round up or to round down. It is best to have a rule that will round down half of the time and round up half of the time. One widely used rule is to round to the even digit, since there is a 50% chance that any digit will be even. For example, 2.5 would be rounded to 2, and 3.5 would be rounded to 4. We will use this rule. An equally valid procedure that is apparently not generally used would be to toss a coin and round up if the coin comes up "heads" and to round down if it comes up "tails."

Example 1.3. Round the following numbers to four significant digits:

(a) 0.2468985

$$0.2468985 \approx 0.2469.$$

(b) 78955

$$78955 \approx 7896.$$

Exercise 1.4. Round the following numbers to three significant digits:

(a) 123456789.
(b) 46.45.

1.6.3 Significant Digits in a Calculated Quantity

The number of significant digits in a calculated quantity depends on the number of significant digits of the variables used to calculate it and on the operations used. We state some rules:

Multiplication and Division

For a product of two or more factors, the rule is that the product will have the same number of significant digits as the factor with the fewest significant digits. The same rule holds for division.

Example 1.4. Find the volume of a rectangular object whose length is given as 7.78 m, whose width is given as 3.486 m, and whose height is 1.367 m.

Using a calculator that displays eight digits after the decimal point, we obtain

$$\begin{aligned} V &= (7.78 \text{ m})(3.486 \text{ m})(1.367 \text{ m}) \\ &= 37.07451636 \text{ m}^3 \approx 37.1 \text{ m}^3. \end{aligned}$$

We round the volume to three significant digits, since the factor with the fewest significant digits has three significant digits.

Example 1.5. Compute the smallest and largest values that the volume in the previous example might have and determine whether the answer given in the example is correctly stated.

The smallest value that the length might have is 7.775 m, and the largest value that it might have is 7.785 m. The smallest possible value for the width is 3.4855 m and the largest value is 3.4865 m. The smallest possible value for the height is 1.3665 m and the largest value is 1.3675 m. The minimum value for the volume is

$$\begin{aligned} V_{\text{min}} &= (7.775 \text{ m})(3.4855 \text{ m})(1.3665 \text{ m}) \\ &= 37.0318254562 \text{ m}^3. \end{aligned}$$

The maximum value is

$$\begin{aligned} V_{\text{max}} &= (7.785 \text{ m})(3.4865 \text{ m})(1.3675 \text{ m}) \\ &= 37.1172354188 \text{ m}^3. \end{aligned}$$

Obviously, all of the digits beyond the first three are insignificant. However, in this case there is some chance that 37.0 m^3 might be closer to the actual volume than is 37.1 m^3. *We will still consider a digit to be significant if it might be incorrect by* ± 1. If the last significant digit obtained by our rule is a1, most people will consider one more digit to be significant.

Exercise 1.5. Find the pressure P of a gas obeying the ideal gas equation

$$PV = nRT,$$

if the volume V is 0.200 m^3, the temperature T is 298.15 K, and the amount of gas n is 1.000 mol. Take the smallest and largest values of each variable and verify your number of significant digits. Note that since you are dividing by V the smallest value of the quotient will correspond to the largest value of V.

Addition and Subtraction

The rule of thumb for significant digits in addition or subtraction is that for a digit to be significant, it must arise from a significant digit in every term of the sum or difference. You must examine each column in the addition.

Example 1.6. Determine the combined length of two objects, one of length 0.783 m and one of length 17.3184 m.

We make the addition:

$$0.788 \text{ m} + 17.3184 \text{ m} = 18.1064 \text{ m} \approx 18.106 \text{ m}.$$

The fourth digit after the decimal point in the sum could be significant only if that digit were significant in every term of the sum. The first number has only three significant digits after the decimal point. We must round the answer to 18.106 m. Even after this rounding, we have obtained a number with five significant digits while one of our terms has only three significant digits.

Significant Digits with Other Operations

With exponentials and logarithms, the function might be so rapidly varying that no simple rule is available. In this case, it is best to calculate the smallest and largest values that might occur.

Example 1.7. Calculate the following to the proper numbers of significant digits: $625.4 \times e^{12.15}$.

We find the values corresponding to the largest and smallest values of the exponential:

$$\begin{aligned} e^{12.155} &= 1.9004 \times 10^5, \\ e^{12.165} &= 1.9195 \times 10^5, \end{aligned}$$

so that

$$e^{12.15} \approx 1.91 \times 10^5,$$

$$625.4 \times e^{12.15} = 625.4 \times 1.91 \times 10^5 = 1.19 \times 10^8.$$

The exponential function is so rapidly varying for large values of its argument that we have only three significant digits, even though we started with four significant digits.

Exercise 1.6. Calculate the following to the proper numbers of significant digits:

(a) 17.13 + 14.6751 + 3.123 + 7.654 − 8.123.
(b) ln (0.000123).

PROBLEMS

1. Find the number of inches in 1.000 m.
2. Find the number of meters in 1.000 mile and the number of miles in 1.000 km, using the definition of the inch.
3. Find the speed of light in miles per second.
4. Find the speed of light in miles per hour.
5. A furlong is exactly one-eighth of a mile and a fortnight is exactly 2 weeks. Find the speed of light in furlongs per fortnight, using the correct number of significant digits.
6. The distance by road from Memphis, Tennessee to Nashville, Tennessee is 206 mi. Express this distance in meters and in kilometers.
7. A US gallon is defined as 231.00 cubic in.

(a) Find the number of liters in one gallon.
(b) The volume of 1.0000 mol of an ideal gas at 25.00 °C (298.15 K) and 1.0000 atm is 24.466 l. Express this volume in gallons and in cubic feet.

8. In the USA, footraces were once measured in yards and at one time, a time of 10.00 s for this distance was thought to be unattainable. The best runners now run 100 m in 10 s or less. Express 100 m in yards, assuming three significant digits. If a runner runs 100.0 m in 10.00 s, find his time for 100 yd, assuming a constant speed.
9. Find the average length of a century in seconds and in minutes. Use the rule that a year ending in 00 is not a leap year unless the year is divisible by 400, in which case it is a leap year. Therefore, in four centuries there will by 97 leap years. Find the number of minutes in a microcentury.
10. A light year is the distance traveled by light in one year:

(a) Express this distance in meters and in kilometers. Use the average length of a year as described in the previous problem. How many significant digits can be given?
(b) Express a light year in miles.

11. The *Rankine temperature scale* is defined so that the Rankine degree is the same size as the Fahrenheit degree, and absolute zero is 0 °R, the same as 0 K:

(a) Find the Rankine temperature at 0.00 °C.
(b) Find the Rankine temperature at 0.00 °F.

12. The volume of a sphere is given by

$$V = \frac{4}{3}\pi r^3,$$

where V is the volume and r is the radius. If a certain sphere has a radius given as 0.005250 m, find its volume, specifying it with the correct number of digits. Calculate the smallest and largest volumes that the sphere might have with the given information and check your first answer for the volume.
13. The volume of a right circular cylinder is given by

$$V = \pi r^2 h,$$

where r is the radius and h is the height. If a right circular cylinder has a radius given as 0.134 m and a height given as 0.318 m, find its volume, specifying it with the correct number of digits. Calculate the smallest and largest volumes that the cylinder might have with the given information and check your first answer for the volume.
14. The value of an angle is given as 31°. Find the measure of the angle in radians. Find the smallest and largest values that its sine and cosine might have and specify the sine and cosine to the appropriate number of digits.
15. Some elementary chemistry textbooks give the value of R, the ideal gas constant, as 0.08211 atm $K^{-1}mol^{-1}$.

(a) Obtain the value of R in l atm K^{-1} mol^{-1} to five significant digits.
(b) Calculate the pressure in atmospheres and in (N m^{-2} Pa) of a sample of an ideal gas with

$$n = 0.13678 \text{ mol}, \quad V = 10.000 \text{ l}, \quad T = 298.15 \text{ K}.$$

16. The van der Waals equation of state gives better accuracy than the ideal gas equation of state. It is

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT,$$

where a and b are parameters that have different values for different gases and where $V_m = V/n$, the molar volume. For carbon dioxide, $a = 0.3640$ Pa m^6 mol^{-2}, $b = 4.267 \times 10^{-5}$ m^3 mol^{-1}. Calculate the pressure of carbon dioxide in pascals, assuming that $n = 0.13678$ mol, $V = 10.00$l, and $T = 298.15$ K. Convert your answer to atmospheres and torr.

17. The *specific heat capacity* (specific heat) of a substance is crudely defined as the amount of heat required to raise the temperature of unit mass of the substance by 1 degree Celsius (1 °C). The specific heat capacity of water is 4.18 $\mathrm{J\,°C^{-1}g^{-1}}$. Find the rise in temperature if 100.0 J of heat is transferred to 1.000 kg of water.

18. The volume of a cone is given by

$$V = \frac{1}{3}\pi r^2 h,$$

where h is the height of the cone and r is the radius of its base. Find the volume of a cone if its radius is given as 0.443 m and its height is given as 0.542 m.

19. The volume of a sphere is equal to $\frac{4}{3}\pi r^3$ where r is the radius of the sphere. Assume that the earth is spherical with a radius of 3958.89 miles. (This is the radius of a sphere with the same volume as the earth, which is flattened at the poles by about 30 miles.) Find the volume of the earth in cubic miles and in cubic meters. Using a value of π with at least six digits give the correct number of significant digits in your answer.

20. Using the radius of the earth in the previous problem and the fact that the surface of the earth is about 70% covered by water, estimate the area of all of the bodies of water on the earth. The area of a sphere is equal to four times the area of a great circle, or $4\pi r^2$, where r is the radius of the sphere.

21. The *hectare* is a unit of land area defined to equal exactly 10,000 $\mathrm{m^2}$, and the acre is a unit of land area defined so that 640 acre equals exactly one square mile. Find the number of square meters in 1.000 acre, and find the number of acres equivalent to 1.000 ha.

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Chapter 2

Mathematical Functions

Principal Facts and Ideas

- A mathematical function is a rule that gives a value of a dependent variable that corresponds to specified values of one or more independent variables.
- A function can be represented in several ways, such as by a table, a formula, or a graph.
- Except for isolated points, the mathematical functions found in physical chemistry are single-valued.
- Except for isolated points, the mathematical functions that occur in physical chemistry are continuous.
- Thermodynamic theory and quantum-mechanical theory specify the number of independent variables for the functions that occur in these disciplines.

Objectives

After studying this chapter, you should:

- understand the concept of a mathematical function and the roles of independent and dependent variables;
- understand the concept of continuity;
- be familiar with functions that commonly appear in physical chemistry problems.

2.1 MATHEMATICAL FUNCTIONS IN PHYSICAL CHEMISTRY

In thermodynamics, the variables involved are governed by mathematical functions. In quantum mechanics all information about the state of a system is contained in a mathematical function called a *wave function* or *state function*. In reaction kinetics, the concentrations of reactants and products are described by mathematical functions of time.

A mathematical function of one independent variable is a rule that generates a unique value of a dependent variable from a given value of an independent variable. It is as though the function says, "You give me a value of the independent variable, and I'll give you the corresponding value of the dependent variable." A simple example of a function is a table with values of the independent variable in one column and corresponding values of the dependent variable in the adjacent column. A number in the first column is uniquely associated with the value on the same line of the second column. However, this is a limited kind of function, which provides values of the dependent variable only for the values in the table. A more general representation might be a formula or a graph, which could provide a value of the dependent variable for any relevant value of the independent variable.

2.1.1 Functions in Thermodynamics

Many of the mathematical functions that occur in physical chemistry have several independent variables. In this case, a value of each of the independent variables must be given to obtain the corresponding value of the dependent variable. Thermodynamic theory implies the following behavior of equilibrium macroscopic systems (systems containing many atoms or molecules):

- Macroscopic thermodynamic variables such as temperature, pressure, volume, density, entropy, energy, and so on, can be dependent or independent variables in mathematical functions.
- Thermodynamic theory governs the number of independent variables, which depends on the conditions. You can generally choose which variables are independent.
- The mathematical functions governing the thermodynamic variables are single-valued, except possibly at isolated points. This means that for a given set of values of the independent variables, one and only one value of the dependent variable occurs.

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- The mathematical functions governing the thermodynamic variables are continuous, except possibly at isolated points.

2.1.2 Functions in Quantum Mechanics

The principal mathematical functions in quantum mechanics are *wave functions* (also called *state functions*) , which have the properties:

- All of the information about the state of a system is contained in a wave function.
- The most general wave functions are functions of coordinates and of time.
- Time-independent wave functions also occur that are functions only of coordinates.
- The wave functions are single-valued and finite.
- The wave functions are continuous.

2.1.3 Function Notation

A mathematician would write the following expression for a dependent variable y that depends on an independent variable x:

$$y = f(x) \tag{2.1}$$

using the letter f to represent the function that provides values of y. Chemists usually follow a simpler policy, writing the same symbol for the dependent variable and the function. For example, representing the pressure as a function of temperature we would write

$$P = P(T), \tag{2.2}$$

where the letter P stands both for the pressure and for the function that provides values of the pressure.

2.1.4 Continuity

If a function is *continuous*, the dependent variable does not change abruptly for a small change in the independent variable. If you are drawing a graph of a continuous function, you will not have to draw a vertical step in your curve. We define continuity with a *mathematical limit*. In a limiting process, an independent variable is made to approach a given value, either from the positive side or the negative side. We say that a function $f(x)$ is continuous at $x = a$ if

$$\lim_{x \to a^+} f\left(x\right) = \lim_{x \to a^-} f(x) = f(a), \tag{2.3}$$

where $f(a)$ is the unique value of the function at $x = a$. The first expression represents causing x to approach the value a from the positive side, and the second expression represents causing x to approach the value a from the negative side. The function is continuous at $x = a$ if as x draws close to a from either direction, $f(x)$ smoothly draws close to the finite value $f(a)$ that the function has at $x = a$. If $f(x)$ approaches one finite value when x approaches a from the negative side and a different finite value when x approaches a from the negative side, we say that the function has a *finite step discontinuity* or*finite jump discontinuity* at $x = a$. Finite step discontinuities are sometimes called *ordinary discontinuities*. In some cases, a function becomes larger and larger in magnitude without bound as x approaches a. We say that the function *diverges* at this point, or that it is *divergent*. For example, the function $1/x$ becomes larger and larger in the negative direction if x approaches 0 from the positive side. It is negative and becomes larger and larger in magnitude if x approaches 0 from the positive direction. Some other functions can diverge in the same direction when the argument of the function approaches some value from either direction. The function $1/x^2$ diverges in the positive direction as x approaches zero from either direction. An infinite discontinuity is sometimes called a *singularity*. Some functions that represent physical variables are continuous over the entire range of values of the independent variable. In other cases, they are *piecewise continuous*. That is, they are continuous except at one or more isolated points, at which discontinuities in the function occur.

2.1.5 Graphs of Functions

One convenient way to represent a function of one variable is with a graph. We plot the independent variable on the horizontal axis and plot the dependent variable on the vertical axis. The height of the curve in the graph represents the value of the dependent variable. A rough graph can quickly show the general behavior of a function. An accurate graph can be read to provide the value of the dependent variable for a given value of the independent variable.

Figure 2.1 shows schematically the density of a pure substance at equilibrium as a function oftemperature at fixed pressure. The density is piecewise continuous. There is a large step discontinuity at the boiling temperature, T_b, and a smaller step discontinuity at the freezing temperature, T_f. If the temperature T approaches T_f from the positive side, the density smoothly approaches the density of the liquid at T_f. If T approaches T_f from the negative side, the density smoothly approaches the density of the solid at this temperature. The system can exist either as a solid or as a liquid at the freezing temperature, or the two phases can coexist, each having a different value of its density. The density is not single-valued at the freezing temperature. A similar step discontinuity occurs at the boiling temperature T_b. At this temperature the liquid and gas phases can coexist with different densities.

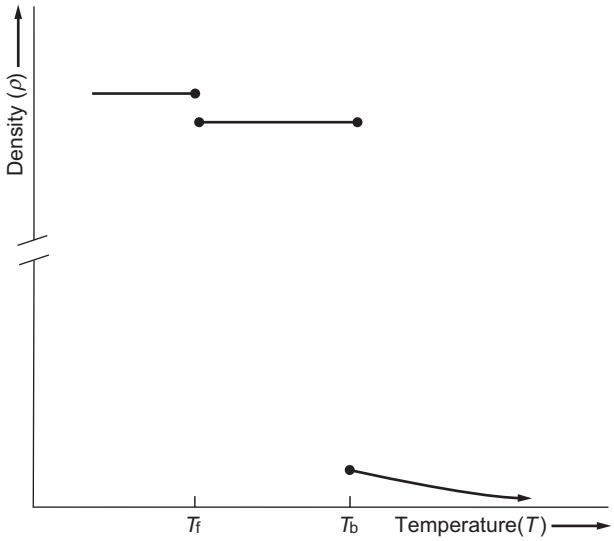


FIGURE 2.1 The density of a pure substance as a function of temperature (schematic).

Graphing with Excel

A spreadsheet such as Excel® can perform various operations on sets of items that are displayed in the form of a table. Microsoft Excel® is sold as a component of Microsoft Office®, which also includes Microsoft Word and Power Point. There are two principal competitors to Excel, called Lotus 1–2-3® and Claris Works®. There is also a suite of programs similar to Microsoft Office called Open Office, which can be downloaded without cost. Our description applies to Excel 2010 using the Windows operating system. Previous versions were called Excel 2003, 2000, 1998, 4.0, 3.0, and so on, and there are some differences in the procedure with the other versions, and with a Macintosh computer.

When you first open the Excel program, a window is displayed on the screen with a number of rectangular areas called cells arranged in rows and columns. This window is called a *worksheet*. Across the top of the window are nine labels: "File," "Home," "Insert," "Page Layout," "Formulas," "Data," "Review," "View," and "Add-in." Clicking on any label produces a different menu with the label in an area that resembles the tab on a file folder. We will refer to the labels as "tabs." The rows in the worksheet are labeled by numbers and the columns are labeled by capital letters. Any cell can be specified by giving its column and its row (its address). For example, the address of the cell in the third row of the second column is B3. Any cell can be selected by using the arrow buttons on the keyboard or by moving the mouse until the cursor is in the desired cell and then clicking the left mouse button.

After selecting a cell, you can type one of three kinds of information into the cell: a number, some text, or a formula. For example, one might want to use the top cell in each column for a label for that column. One would first select the top cell in a given column and then type the label for that column. As the label is typed, it appears in a line above the cells. It is then entered into the cell by pressing the "Enter" key in the main keyboard (labeled "Return" on some keyboards). A number is entered into a cell in the same way. To enter a number but treat it as text, precede the number with an apostrophe (', a single quotation mark).

To enter a formula, type an equal sign followed by the formula, using ordinary numbers, addresses of cells, symbols for predefined functions, and symbols for operations. If you need a number stored in another cell in a formula, type the address of that cell into the formula in place of the number. The symbol * (asterisk) is used for multiplication, / (slash) is used for division, + (plus) is used for addition, and − (minus) is used for subtraction. The caret symbol (^) is used for powers. All symbols are typed on the same line. For example, $(3.26)^{3/2}$ would be represented by 3.26^1.5. Don't use 3.26^3/2 to represent $3.26^{3/2}$ since the computer carries out operations in a predetermined sequence. Powers are carried out before multiplications and divisions, so the computer would compute 3.26^3 and then divide by 2. Since the formula must be typed on a single line, parentheses are used as necessary to make sure that the operations are carried out correctly. The rule is that all operations inside a pair of parentheses are carried out before being combined with anything else. Other operations are carried out from left to right, with multiplications and divisions carried out before additions and subtractions. If there is any doubt about which operations are carried out first, use parentheses to make the formula unambiguous. Any number of parentheses can be used, but make sure that every left parenthesis has a right parenthesis paired with it.

A number of predefined functions can be included in formulas. Table 2.1 includes some of the abbreviations that are used. The argument of a function is enclosed in parentheses in place of the ellipsis (· · ·).

TABLE 2.1 Abbreviations in Excel

Abbreviation	Function
SIN(· · ·)	sine
COS(· · ·)	cosine
ASIN(· · ·)	Inverse sine
ACOS(· · ·)	Inverse cosine
ABS(· · ·)	Absolute value
EXP(· · ·)	Exponential
LOG(· · ·)	Common logarithm (base 10)
LN(· · ·)	Natural logarithm (base *e*)

If you want cell C3 to contain the natural logarithm of the number presently contained in cell B2, you would place the cursor on cell C3 and click on it with the left mouse button. and then type =LN(B2). Lower-case letters can also be used and LOG10(···) can be used for the common logarithm. The argument of a trigonometric function must be expressed in radians. An arithmetic expression can be used as the argument and will automatically be evaluated before the function is evaluated. These rules are similar to those used in the BASIC and FORTRAN programming languages and in Mathematica®.

After the formula is typed, one enters it into the cell by pressing the "Enter" key in the main keyboard. When a formula is entered into a cell, the computer will automatically calculate the appropriate number from whatever constants and cell contents are specified and will display the numerical result in the cell. If the value of the number in a cell is changed, any formulas in other cells containing the first cell's address will automatically be recalculated.

Example 2.1. Enter a formula into cell C1 to compute the sum of the number in cell A1 and the number in cell B2, divide by 2, and take the common logarithm of the result.

We select cell C1 and type the following:

$$= \mathrm{LOG}((\mathrm{A1} + \mathrm{B2})/2).$$

We then press the "Enter" key (labeled "Return" on some keyboards). The numerical answer will appear in cell C1.

The SUM command will compute the sum of several adjacent numbers in the same column. For example, to compute the sum of the contents of the cells A2, A3, and A4 and place the sum in cell D2, you would put the cursor in cell D2 and type =SUM(A2:A4). If you want the sum of the contents of all cells from A2 to A45, you would type =SUM(A2:A45). A colon (:) must be placed between the addresses of the first and last cells.

Exercise 2.1. Enter a formula into cell D2 that will compute the mean of the numbers in cells A2, B2, and C2.

If you move a formula from one cell to another, any addresses entered in the formula will change. For example, say that the address A1 and the address B2 were typed into a formula placed in cell C1. If this formula is copied and pasted into another cell, the address A1 is replaced by the address of whatever cell is two columns to the left of the new location of the formula. The address B2 is replaced by the address of whatever cell is one column to the left and one row below the new location of the formula. Such addresses are called *relative addresses* or *relative references*. This feature is very useful, but you must get used to it. If you want to move a formula to a new cell but still want to refer to the contents of a particular cell, put a dollar sign ($) in front of the column letter and another dollar sign in front of the row number. For example, A1 would refer to cell A1 no matter what cell the formula is placed in. Such an address is called a *absolute address* or an *absolute reference*.

There is a convenient way to copy a formula into part of a column. Type a formula with the cursor in some cell and then press the "Enter" key to enter the formula into that cell. Then drag the cursor down the column (while holding down the left mouse button) including the cell containing the formula and moving down as far as needed. Then choose the "Fill" command in the "Edit" menu and choose "Down" from a small window that appears. You can also hold down the "Ctrl" key and type the letter "d". When you do this, the selected cells are all "filled" with the formula. The formulas in different cells will refer to different cells according to the relative addressing explained above. A similar procedure is used to fill a portion of a row by entering the formula in the left-most cell of a portion of a row, selecting the portion of the row, and using the "Fill" command in the "Edit" menu and choosing "Right" in the next window, or alternatively by holding down the "Ctrl" key and typing the letter "r". The same procedures can be used to fill a column or a row with the same number in every cell. You can also put a sequence of equally spaced values in a column. Say that you want to start with a zero value in cell A1 and to have values incremented by 0.05 as you move down the following 20 cells in column A. You select cell A1, type in the value 0, and press the "Enter" key. You then select cell A2, type in =A1 + 0.05, and press the "Enter" key. You place the cursor on cell A2 and drag it down to cell A21 (keeping the left mouse button depressed). You then select "Fill Down" or type the letter "d" key while pressing the "Ctrl" key.

A block of cells can be selected by moving the cursor to the upper left cell of the block and then moving it to the opposite corner of the block while holding down the left mouse button ("dragging" the cursor). You can also drag the cursor in the opposite direction. The contents of the cell or block of cells can then be cut or copied into the clipboard, using the "Cut" command or the "Copy" command under the "Home" tab. The contents of the clipboard can be pasted into a new location. One selects the upper left cell of the new block of cells and then uses the "Paste" command under the "Home" tab to paste the clipboard contents into the workbook. If you put something into a set of cells and want to remove it, you can select the cells and then press the "Delete" key.

Excel can use routines called "Macros" that can be called inside the spreadsheet. These routines can be written in a version of the BASIC programming language called "Visual Basic." Instructional websites detailing the use of

Visual Basic can be found on the Internet by searching for Visual Basic in a search engine such as Google. Textbooks are also available. Macros can also be obtained from other sources, such as Internet websites.

Excel can be used to produce graphs of various kinds (Excel refers to graphs as "charts"). To construct a graph of a function of one independent variable, you place values of the independent variable in one column and the corresponding values of the dependent variable in the column immediately to the right of this column. If you require a graph with more than one curve, you load the values of the independent variable in one column, the values of the first function in the column to the right of this column, the values of the second function into the next column, and so on. If appropriate, use formulas to obtain values of the dependent variables. Here is the procedure:

1. Select the columns by dragging the mouse cursor over them.
2. Click on the "Insert" tab. A set of icons appears. Click on the "Scatter" icon. Five icons appear, allowing you to choose whether you want a smooth curve or line segments through the points, with or without data points. We assume that you choose the option with a smooth curve showing the data points. Click on the "Layout" tab in the "Chart Tools" Menu. In this menu, you can choose whether to add vertical gridlines and can label the axes and enter a title for the graph. You can delete or edit the "Legend," which is a label at the right of the graph. You can change the size of the graph by clicking on a corner of the graph and dragging the cursor while holding down the left mouse button. You can double-click on one of the numbers on an axis and get a menu allowing you to enter tick-marks on the axis, and change the range of values on the axis.
3. You can print the graph by using the "Print" command under the "File" tab or by holding down the "Ctrl" key and typing the letter "p". The printed version will be shown on the screen. If it is acceptable, click on the "print" icon.

2.2 IMPORTANT FAMILIES OF FUNCTIONS

A *family of functions* is a set of related functions. A family of functions is frequently represented by a single formula that contains other symbols besides the one for the independent variable. These quantities are called *parameters*. The choice of a value for each parameter specifies a member of the family of functions.

2.2.1 Linear Functions

The following formula represents the family of *linear functions:*

$$y = mx + b. \tag{2.4}$$

Linear functions are also called *first-degree polynomials*. We have a different function for each value of the parameter m and the parameter b. The graph of each such function is a straight line. The constant b is called the *intercept*. It equals the value of the function at $x = 0$. The constant m is called the *slope*. It gives the steepness of the line, or the relative rate at which the dependent variable changes as the independent variable varies. A one-unit change in x produces a change in y equal to m.

Figure 2.2 shows a graph representing a linear function.

Two values of x, called x_1 and x_2, are indicated, as are their corresponding values of y, called y_1 and y_2. A line is drawn through the two points. If $m > 0$, then $y_2 > y_1$ and the line slopes upward to the right. If $m < 0$, then $y_2 < y_1$ and the line slopes downward to the right. If a line is horizontal, the slope is equal to zero.

Example 2.2. For a linear function let y_1 be the value of y corresponding to x_1 and y_2 be the value of y corresponding to x_2. Show that the slope is given by

$$m = \frac{y_2 - y_1}{x_2 - x_1} = \frac{\Delta y}{\Delta x},$$

where we introduce the common notation for a difference:

$$\Delta x = x_2 - x_1,$$
$$\Delta y = y_2 - y_1,$$

$$y_2 - y_1 = mx_2 + b - (mx_1 + b) = m(x_2 - x_1)$$

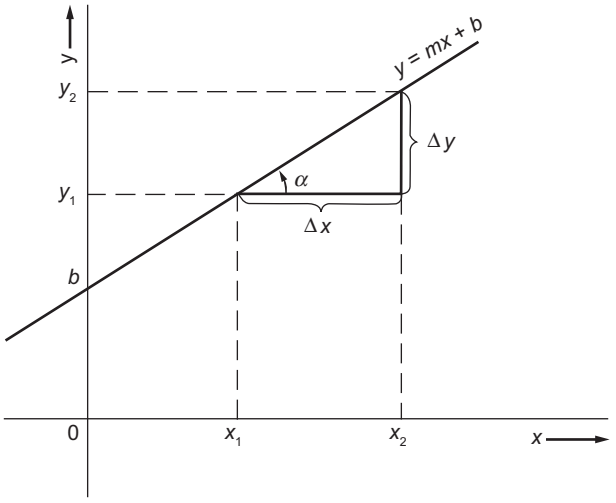


FIGURE 2.2 The graph of the linear function $y = mx + b$.

or

$$m = \frac{y_2 - y_1}{x_2 - x_1} = \frac{\Delta y}{\Delta x}.$$

2.2.2 Quadratic Functions

Another important family of functions is the *quadratic function* or *second-degree polynomial*:

$$y = ax^2 + bx + c. \tag{2.5}$$

The graph of a function from this family is a *parabola*. Figure 2.3 depicts the parabola representing the function

$$y(x) = x^2 - 3x - 4.$$

Notice that the curve representing the parabola rises rapidly on both sides of the minimum.

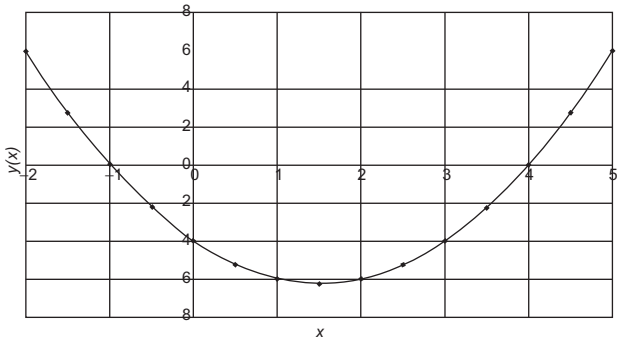


FIGURE 2.3 The graph of the quadratic function $y = x^2 - 3x - 4$.

2.2.3 Cubic Functions

A cubic function, or third-degree polynomial, can be written in the form

$$y(x) = ax^3 + bx^2 + cx + d, \tag{2.6}$$

where a, b, c, and d represent constants.

Exercise 2.2. Use Excel or Mathematica to construct a graph representing the function

$$y(x) = x^3 - 2x^2 + 3x + 4.$$

2.2.4 Logarithms

A logarithm is an exponent. We write

$$x = a^y. \tag{2.7}$$

The constant a is called the *base of the logarithm* and the exponent y is called the *logarithm of x to the base a* and is denoted by

$$y = \log_a (x). \tag{2.8}$$

We take a to be positive so that only positive numbers possess real logarithms.

Common Logarithms

If the base of logarithms equals 10, the logarithms are called *common logarithms:* If $10^y = x$, then y is called the common logarithm of x, denoted by $\log_{10}(x)$. The subscript 10 is sometimes omitted, but this can cause confusion. For integral values of x, it is easy to generate the following short table of common logarithms:

x	$y = \log_{10}(x)$	x	$y = \log_{10}(x)$
1	0	0.1	−1
10	1	0.01	−2
100	2	0.001	−3
1000	3	0.0001	−4

Exponents are not required to be integers, so logarithms are not required to be integers.

Example 2.3. Find the common logarithm of $\sqrt{10}$.

$$\left(\sqrt{10}\right)^2 = 10.$$

We use the fact about exponents

$$(a^x)^z = a^{xz}.$$

Since10 is the same thing as 10^1,

$$\sqrt{10} = 10^{1/2} = 3.162277\cdots.$$

Therefore

$$\log_{10}\left(\sqrt{10}\right) = \log_{10}(3.162277\cdots) = \frac{1}{2} = 0.5000.$$

Exercise 2.3. Generate the negative logarithms in the short table of common logarithms.

Before the widespread use of electronic calculators, extensive tables of logarithms with up to seven or eight significant digits were used when a calculation required more significant digits than a slide rule could provide. For example, to multiply two numbers together, one would look up the logarithms of the two numbers, add the logarithms, and then look up the *antilogarithm* of the sum (the number possessing the sum as its logarithm).

Natural Logarithms

The other commonly used base of logarithms is a transcendental irrational number called e and equal to

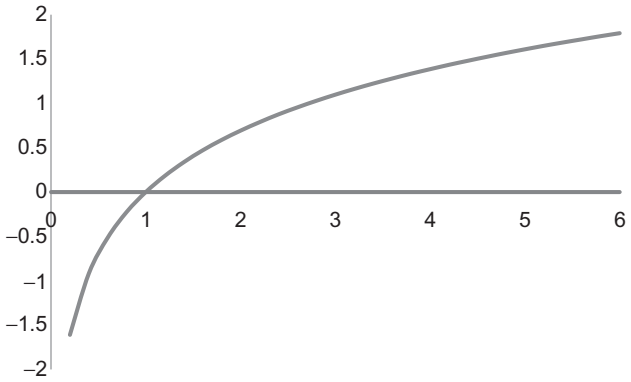


FIGURE 2.4 A graph representing the natural logarithm of x.

$2.7182818284\cdots$.[1] The definition of e is

$$e = \lim_{n\to\infty}\left(1+\frac{1}{n}\right)^n = 2.7182818\ldots \text{ (definition)}. \tag{2.9}$$

The "$\lim_{n\to\infty}$" notation means that larger and larger values of n are taken. In this case a stable value of the quantity is approached in the limit.

Exercise 2.4. Using a calculator or a spreadsheet, evaluate the quantity $(1+\frac{1}{n})^n$ for several integral values of n ranging from 1 to 1,000,000. Notice how the value approaches the value of e as n increases and determine the value of n needed to provide four significant digits.

Logarithms to the base e are called *natural logarithms*:

$$\boxed{\text{If } e^y = x \quad \text{then } y = \log_e(x) = \ln(x)}. \tag{2.10}$$

The notation $\ln(x)$ is more common than the notation $\log_e(x)$ for natural logarithms. Natural logarithms are also called *Napierian logarithms*.[2] Unfortunately, some mathematicians use the symbol $\log(y)$ without a subscript for the natural logarithm of y. Chemists frequently use the symbol $\log(y)$ without a subscript for common logarithms and the symbol $\ln(y)$ for natural logarithms. It is probably best to use $\log_{10}(x)$ for the common logarithm of x and $\ln(x)$ for the natural logarithm of x.

Figure 2.4 illustrates two facts about logarithms:

- For values of the argument less than unity, the logarithm is a rapidly changing function.
- For values of the argument much greater than unity, the logarithm is a slowly varying function.

[1] The base of natural logarithms, e, is named after Leonhard Euler, 1707–1783, a great Swiss mathematician.

[2] Napierian logarithms are named after John Napier, 1550–1617, a Scottish landowner, theologian, and mathematician, who was one of the inventors of logarithms.

If the common logarithm of a number is known, its natural logarithm can be computed as follows:

$$e^{\ln(y)} = 10^{\log_{10}(y)} = \left(e^{\ln(10)}\right)^{\log_{10}(y)} = e^{\ln(10)\log_{10}(y)}. \tag{2.11}$$

The natural logarithm of 10 is equal to $2.302585\ldots$, so we can write

$$\boxed{\ln(y) = \ln(10)\log_{10}(y) = (2.30258509\ldots)\log_{10y}(y)}. \tag{2.12}$$

In order to remember Eq. (2.12) correctly, remember that since e is smaller than 10, the natural logarithm is larger than the common logarithm.

Exercise 2.5. Without using a calculator or a table of logarithms, find the following:

(a) $\ln(100.000)$,
(b) $\ln(0.0010000)$,
(c) $\log_{10}(e)$.

Logarithm Identities

Table 2.2 lists some identities involving exponents and logarithms. These identities hold for logarithms to any base.

TABLE 2.2 Properties of Exponents and Logarithms

Exponent fact	Logarithm fact
$a^0 = 1$	$\log_a(1) = 0$
$a^{1/2} = \sqrt{a}$	$\log_a(\sqrt{a}) = \frac{1}{2}$
$a^1 = a$	$\log_a(a) = 1$
$a^{x_1}a^{x_2} = a^{x_1+x_2}$	$\log_a(y_1y_2) = \log_a(y_1) + \log_a(y_2)$
$a^{-x} = \frac{1}{a^x}$	$\log_a\left(\frac{1}{y}\right) = -\log_a(y)$
$\frac{a^{x_1}}{a^{x_2}} = a^{x_1-x_2}$	$\log_a\left(\frac{y_1}{y_2}\right) = \log_a(y_1) - \log_a(y_2)$
$(a^x)^z = a^{xz}$	$\log_a(y^z) = z\log_a(y)$
$a^\infty = \infty$	$\log_a(\infty) = \infty$
$a^{-\infty} = 0$	$\log_a(0) = -\infty$

2.2.5 Exponentials

The *exponential function* is the same as raising e (the base of natural logarithms) to a given power. It is denoted either by the usual notation for a power or by the notation $\exp(\cdots)$. If b is a constant and y is the exponential of bx, then

$$y = e^{bx} = \exp(bx). \tag{2.13}$$

Figure 2.5 shows a graph of the exponential function for $b = 1$.

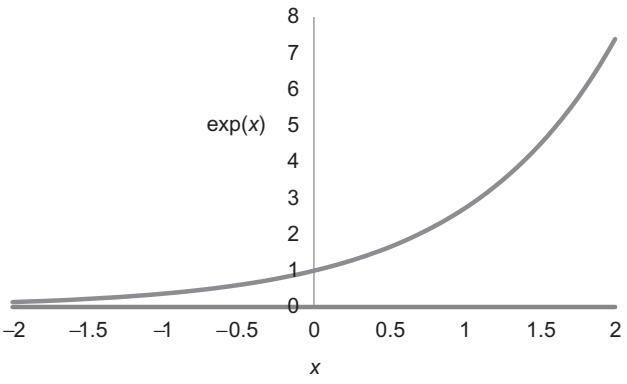


FIGURE 2.5 The exponential function.

There are several important properties of the exponential function, as exhibited in the graph in Figure 2.5.

- For large values of x the exponential function becomes large very rapidly.
- For large negative values of x the exponential function becomes small very rapidly.
- If b is negative, the exponential function decreases to half its value each time x increases by a fixed amount.
- If b is positive, the exponential function doubles each time x increases by a fixed amount.

Exercise 2.6. For a positive value of b find an expression in terms of b for the change in x required for the function e^{bx} to double in size.

An example of the exponential function is in the decay of radioactive isotopes. If $N(t)$ represents the number at time t,

$$N(t) = N(0)e^{-t/\tau}, \tag{2.14}$$

where τ is called the *relaxation time*. It is the time for the number of atoms of the isotope to drop to $1/e = 0.367879\cdots$ of its original value. The time that is required for the number of atoms to drop to half its original value is called the *half-time* or *half-life*, denoted by $t_{1/2}$.

Example 2.4. Show that $t_{1/2}$ is equal to $\tau \ln(2)$.

If $t_{1/2}$ is the half-life, then

$$e^{-t_{1/2}/\tau} = \frac{1}{2}$$

Thus

$$\begin{aligned} \frac{t_{1/2}}{\tau} &= -\ln\left(\frac{1}{2}\right) = \ln(2), \\ t_{1/2} &= \ln(2)\,\tau \approx 0.693147\tau. \end{aligned}$$

Example 2.5. A certain population is growing exponentially and doubles in size each 30.0 years.

(a) If the population includes 4.00×10^6 individuals at $t = 0$, write the formula giving the population after a number of years equal to t.

We let

$$\begin{aligned} \frac{N(30.0y)}{N(0)} &= 2 = e^{kt}, \\ k &= \frac{\ln(2)}{30.0y} = 0.02310y^{-1}, \\ \frac{N(t)}{N(0)} &= \frac{N(t)}{4.00 \times 10^6} = e^{(0.02310y^{-1})t}. \end{aligned}$$

(b) Find the size of the population at $t = 150.0$ years.

$$\begin{aligned} N(150.0y) &= \left(4.00 \times 10^6\right) \exp\left[\left(0.02310y^{-1}\right)\left(150.0y\right)\right] \\ &= 1.28 \times 10^8 \end{aligned}$$

Exercise 2.7. A reactant in a first-order chemical reaction without back reaction has a concentration governed by the same formula as radioactive decay,

$$\left[A\right]_t = \left[A\right]_0 e^{-kt},$$

where $\left[A\right]_0$ is the concentration at time $t = 0$, $\left[A\right]_t$ is the concentration at time t, and k is a function of temperature called the rate constant. If $k = 0.123\ \mathrm{s}^{-1}$ find the time required for the concentration to drop to 21.0% of its initial value.

2.2.6 Trigonometric Functions

The ordinary *trigonometric functions* include the sine, the cosine, the tangent, the cotangent, the secant, and the cosecant. They are sometimes called the *circular trigonometric functions.*

The trigonometric functions can be defined geometrically using a circle, as in Figure 2.6.

This figure shows two angles, α_1 , which is smaller than 90°, and α_2, which is larger than 90° but smaller than 180°. Along the horizontal axis the point C_1 is chosen so that the triangle AB_1C_1 is a right triangle. The radius of the circle, r, forms the *hypotenuse* of the triangle. The vertical side of length y_1 is called the *opposite side* to the angle α_1 and the horizontal side of length x_1 is called the *adjacent side*. We define the trigonometric functions sine, cosine, and tangent of α_1 as follows:

$$\boxed{\sin\left(\alpha_1\right) = \tfrac{y_1}{r} \quad \text{(opposite side over hypotenuse)}}, \tag{2.15}$$

$$\boxed{\cos\left(\alpha_1\right) = \tfrac{x_1}{r} \quad \text{(adjacent side over hypotenuse)}}, \tag{2.16}$$

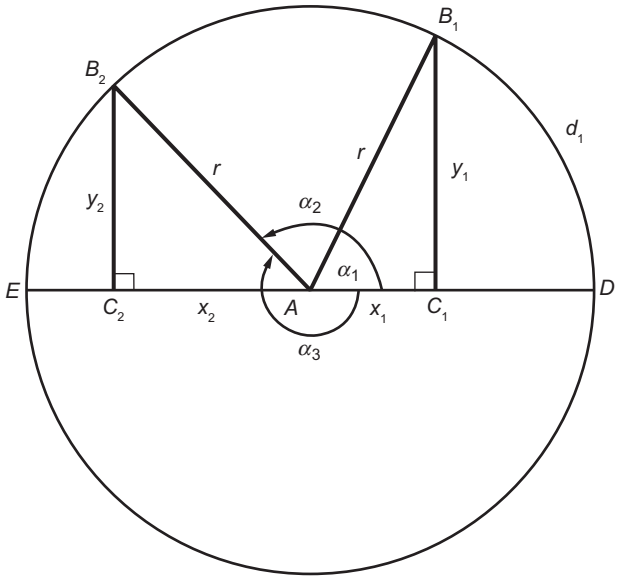


FIGURE 2.6 The figure used in defining trigonometric functions.

$$\boxed{\tan(\alpha_1) = \tfrac{y_1}{x_1} \quad \text{(opposite side over adjacent side)}}, \tag{2.17}$$

$$\boxed{\cot(\alpha_1) = \tfrac{x_1}{y_1} \quad \text{(adjacent side over opposite side)}}, \tag{2.18}$$

$$\boxed{\sec(\alpha_1) = \tfrac{r}{x_1} \quad \text{(hypotenuse over adjacent side)}}, \tag{2.19}$$

$$\boxed{\csc(\alpha_1) = \tfrac{r}{y_1} \quad \text{(hypotenuse over opposite side)}}. \tag{2.20}$$

The trigonometric functions of the angle α_2 are defined in the same way, except that the distance x_2 must be counted as negative, because the point C_2 is to the left of A. If the point B_2 were below A, then y_2 would also be counted as negative. For all values of the angle α, we can write the identities (relations that are valid for values of the variables involved):

$$\csc(\alpha) = \frac{1}{\sin(\alpha)}, \tag{2.21}$$

$$\sec(\alpha) = \frac{1}{\cos(\alpha)}, \tag{2.22}$$

$$\cot(\alpha) = \frac{1}{\tan(\alpha)}. \tag{2.23}$$

There are three common ways to specify the size of an angle (*the "measure" of the angle*). *Degrees* are defined so that a right angle corresponds to 90° (90°), and a full rotation corresponds to 360°. The *grad* is defined so that 100 grad corresponds to a right angle and a full rotation corresponds 400 grad. The measure of an angle in radians is defined to be the length of the arc subtending the angle divided by the radius of the circle. In Figure 2.6, the arc DB_1 subtends the angle α_1, so that in radians

$$\alpha_1 = \frac{d_1}{r}, \tag{2.24}$$

where d_1 is the length of the arc DB_1. The full circle contains 2π radians (2π rad) or 360°, and 1 radian corresponds to $360°/(2\pi) = 57.2957795\cdots°$. The right angle, 90°, is $\pi/2$ radians $= 1.5707963\cdots$ radians ($1.5707963\cdots$ rad). We can express the angle α in terms of radians, degrees, or grad, but must understand which measure is being used. For example, we could write

$$\sin(90°) = \sin(\pi/2). \tag{2.25}$$

This does not look like a correct equation until we understand that on the left-hand side the angle is measured in degrees and on the right-hand side the angle is measured in radians. If you use degrees, you should always include the degree sign (◦) to avoid confusion.

The trigonometric functions illustrate a general property of the functions that we deal with. They are *single-valued*: for each value of the angle α, there is one and only one value of the sine, one and only one value of the cosine, and so on. The sine and cosine functions are continuous everywhere. The tangent, cotangent, secant, and cosecant functions are piecewise continuous (discontinuous only at isolated points, where they diverge).

Trigonometric Identities

There are a number of relations between trigonometric functions that are valid for all values of the given angles. Such relations are said to be *identically true*, or to be *identities*. We first present some identities involving an angle and its negative. A negative angle is measured in the clockwise direction while positive angles are measured in the counterlockwise direction. A figure analogous to Figure 2.6 with a negative angle can be used to show that

$$\boxed{\sin(\alpha) = -\sin(-\alpha)}, \tag{2.26}$$

$$\boxed{\cos(\alpha) = \cos(-\alpha)}, \tag{2.27}$$

$$\boxed{\tan(\alpha) = -\tan(-\alpha)}. \tag{2.28}$$

Equations (2.26) and (2.28) express the fact that the sine and the tangent are *odd functions*. If $f(x)$ is odd function, then

$$f(-x) = -f(x) \text{ (odd function)}. \tag{2.29}$$

The cosine is an *even function*. If $f(x)$ is an even function, then

$$f(-x) = f(x) \text{ (even function)}. \tag{2.30}$$

Figure 2.6 also shows a negative angle α_3. This angle corresponds to the same triangle, and therefore the same trigonometric functions as the positive angle α_2. Since α_3 is equal to $-(2\pi - \alpha_2)$ if the angles are measured in radians, we can write an identity:

$$\sin(\alpha_3) = \sin\left[-\left(2\pi - \alpha_2\right)\right] = \sin\left(\alpha_2 - 2\pi\right) = \sin\left(\alpha_2\right) \tag{2.31}$$

with similar equations for the other trigonometric functions. If an angle is increased by 2π radians (360°), the new angle corresponds to the same triangle as does the old angle, and we can write

$$\boxed{\sin\left(\alpha\right) = \sin(\alpha + 2\pi) = \sin(\alpha + 4\pi) = \cdots}, \tag{2.32}$$

$$\boxed{\cos(\alpha) = \cos(\alpha + 2\pi) = \cos\left(\alpha + 4\pi\right) = \cdots}, \tag{2.33}$$

with similar equations for the other trigonometric functions. The trigonometric functions are *periodic functions* with period 2π. That is, if any integral multiple of 2π is added to the argument, the value of the function is unchanged.

Exercise 2.8. Using a calculator, find the value of the cosine of 15.5° and the value of the cosine of 375.5°. Display as many digits as your calculator is able to display. Check to see if your calculator produces any round-off error in the last digit. Choose another pair of angles that differ by 360° and repeat the calculation. Set your calculator to use angles measured in radians. Find the value of sin (0.3000). Find the value of sin $(0.3000 + 2\pi)$. See if there is any round-off error in the last digit.

A useful trigonometric identity is the famous *theorem of Pythagoras*.[3] Pythagoras drew a figure with three squares such that one side of each square formed a side of the same right triangle. He then proved by geometry that the area of the square on the hypotenuse was equal to the sum of the areas of the squares on the other two sides. In terms of the quantities in Figure 2.6

$$\boxed{x^2 + y^2 = r^2}. \tag{2.34}$$

[3] Pythagoras (ca. 570 BC-ca. 495 BC) was a Greek philosopher, mathematician, and founder of a religious sect.

We divide both sides of this equation by r^2 and use the definitions of the sine and cosine to obtain the very useful identity:

$$\boxed{\left[\sin\left(\alpha\right)\right]^2 + \left[\cos\left(\alpha\right)\right]^2 = \sin^2\left(\alpha\right) + \cos^2\left(\alpha\right) = 1}. \tag{2.35}$$

Notice the common notation for a power of a trigonometric function: the exponent is written after the symbol for the trigonometric function and before the parentheses enclosing the argument. Do not use this notation if the exponent is -1, since this notation is used for the inverse trigonometric functions, which we discuss later.

Exercise 2.9. Using a calculator and displaying as many digits as possible, find the values of the sine and cosine of 49.500°. Square the two values and add the results. See if there is any round-off error in your calculator.

A Useful Approximation

Comparison of Eqs. (2.15) and (2.24) shows that for a fairly small angle, the sine of an angle and the measure of the angle in radians are approximately equal, since the sine differs from the measure of the angle only by having the opposite side in place of the arc length, which is approximately the same size. As the angle is made smaller and smaller, we can write

$$\lim_{\alpha \to 0} \frac{\sin\left(\alpha\right)}{\alpha} = 1 \quad \left(\alpha \text{ measured in radians}\right). \tag{2.36}$$

For small angles, we write as an approximation

$$\alpha \approx \sin\left(\alpha\right) \quad \text{(small values of } \alpha\text{)}, \tag{2.37}$$

where the angle α must be measured in radians. Since the adjacent side of a right triangle is nearly equal to the hypotenuse for small angles, we can also write θ

$$\boxed{\alpha \approx \tan(\alpha) \approx \sin(\alpha) \quad \text{(small values of } \alpha\text{)}}. \tag{2.38}$$

Equations (2.37) and (2.38) are valid for both positive and negative values of α. If you are satisfied with an accuracy of about 1%, you can use Eq. (2.38) for angles with magnitude up to about 0.2 radians (roughly 11°).

Exercise 2.10. Construct an accurate graph of sin (x) and tan (x) on the same graph for values of x from 0 to 0.4 rad and find the maximum value of x for which the two functions differ by less than 1%.

Exercise 2.11. For an angle that is nearly as large as $\pi/2$, find an approximate equality similar to Eq. (2.38) involving $(\pi/2) - \alpha$, cos (α), and cot (α).

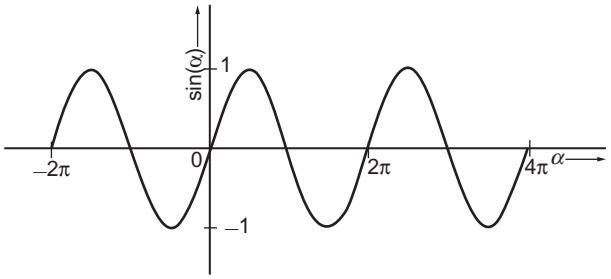


FIGURE 2.7 The sine of an angle.

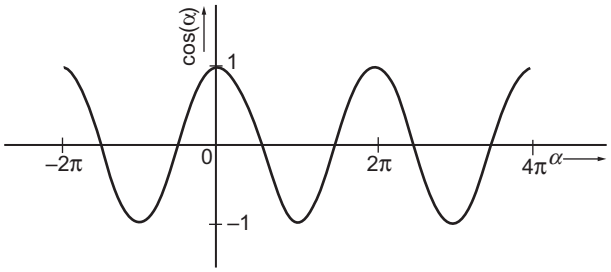


FIGURE 2.8 The cosine of an angle.

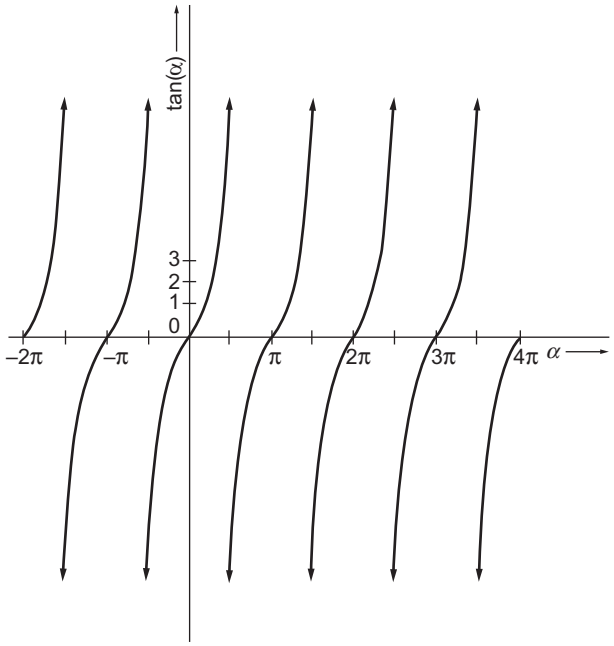


FIGURE 2.9 The tangent of an angle.

General Properties of Trigonometric Functions

To use trigonometric functions easily, you should have a clear mental picture of the way in which the sine, cosine, and tangent depend on their arguments. Figures 2.7, 2.8, and 2.9 show these functions.

The tangent becomes more positive without bound as its argument approaches $\pi/2$ from the left, and becomes more negative without bound as its argument approaches $\pi/2$ from the right. We can write

$$\lim_{\alpha \to \frac{\pi}{2}+} [\tan(\alpha)] = -\infty, \tag{2.39}$$

$$\lim_{\alpha \to \frac{\pi}{2}-} [\tan(\alpha)] = \infty. \tag{2.40}$$

In these equations, the superscript $+$ on the $\pi/2$ in the limit means that the value of α approaches $\pi/2$ from the right. The $-$ superscript in the limit means that α is smaller than $\pi/2$ as it approaches $\pi/2$. The symbol ∞ stands for *infinity*, which is larger than any number that you or anyone else can name. Infinity is sometimes called "*undefined.*"

2.2.7 Inverse Trigonometric Functions

Trigonometric functions define mathematical functions in an inverse way. For example, if

$$y = \sin(x), \tag{2.41}$$

we can define a function to give a value for x as a function of y. We write

$$x = \arcsin(y) \qquad \text{(preferred notation)}. \tag{2.42}$$

This can be read as "x is the angle whose sine is y." The *arcsine* function is also called the *inverse sine* function, and another notation is also common:

$$x = \sin^{-1}(y). \tag{2.43}$$

The -1 superscript indicates an inverse function. It is not an exponent, even though exponents are written in the same position. If you need to write the reciprocal of $\sin(y)$, you should write $[\sin(y)]^{-1}$ to avoid confusion. It is probably better to use the notation of Eq. (2.42) rather than that of Eq. (2.43). The other inverse trigonometric functions such as the inverse cosine and inverse tangent are defined in the same way as the arcsine function.

Since the trigonometric functions are periodic, there are many angles that have the same value of the sine function. In order to make the arcsine in Eq. (2.42) or Eq. (2.43) into a single-valued function, we must restrict the values of x that we consider. With the arcsine function, these values are taken from $-\pi/2$ to $+\pi/2$ and are called the *principal values* of the arcsine function. The principal values of the arctangent and arccosecant functions range from $-\pi/2$ to $+\pi/2$, the same as with the arcsine. The principal values of the arccosine, arccotangent, and arcsecant are taken from 0 to π.

Exercise 2.12. Sketch graphs of the arcsine function, the arccosine function, and the arctangent function. Include only the principal values.

2.2.8 Hyperbolic Trigonometric Functions

These functions are closely related to the exponential function. The *hyperbolic sine* of x is denoted by $\sinh(x)$, and defined by

$$\sinh(x) = \frac{1}{2}(e^x - e^{-x}). \tag{2.44}$$

The *hyperbolic cosine* is denoted by $\cosh(x)$, and defined by

$$\cosh(x) = \frac{1}{2}\left(e^x + e^{-x}\right). \tag{2.45}$$

The hyperbolic trigonometric functions are not periodic. The other hyperbolic trigonometric functions are the *hyperbolic tangent*, denoted by $\tanh(x)$; the *hyperbolic cotangent*, denoted by $\coth(x)$; the *hyperbolic secant*, denoted by $\mathrm{sech}(x)$; and the hyperbolic cosecant, denoted by $\mathrm{csch}(x)$. These functions are given by the identities

$$\tanh(x) = \frac{\sinh(x)}{\cosh(x)}, \tag{2.46}$$

$$\coth(x) = \frac{1}{\tanh(x)}, \tag{2.47}$$

$$\mathrm{sech}(x) = \frac{1}{\cosh(x)}, \tag{2.48}$$

$$\mathrm{csch}(x) = \frac{1}{\sinh(x)}. \tag{2.49}$$

Figure 2.10 shows the hyperbolic sine and hyperbolic cosine for values of x from 0 to 3. Note that the values of the hyperbolic sin and the hyperbolic cosine do not necessarily lie between -1 and 1 as do the values of the circular sine and cosine functions and that both functions approach $e^x/2$ for large values of x. The hyperbolic trigonometric functions are available in Excel.

Exercise 2.13. Make a graph of $\tanh(x)$ and $\coth(x)$ on the same graph for values of x ranging from 0.1 to 3.0.

2.2.9 Significant Digits in Logarithms, Exponentials, and Trigonometric Functions

Determining which digits are significant is not so easy as with these functions as with arithmetic operations. Rules of thumb can be found,[4] but it is best to do the operation with the smallest and the largest values that the variable on which you operate can have (incrementing and decrementing the nominal value). Consider the logarithm function: For values of the argument less than unity, the logarithm function is rapidly varying; for large values of the argument, the logarithm function is slowly varying. The exponential function has an opposite behavior: For values of the argument less than unity, the exponential function is slowly varying; for large values of its argument, the exponential function is rapidly varying. Determining the number of significant digits in a calculation with trigonometric functions also often requires incrementing and decrementing.

Example 2.6. Calculate the following. Determine the correct number of significant digits:

(a) $\ln(56781)$

$$\ln(56781.5) = 10.9469658474,$$
$$\ln(56780.5) = 10.9469482359,$$

Therefore,

$$\ln(56781) = 10.94695.$$

In this case, a number with five significant digits had a logarithm with seven significant digits.

(b) $e^{-9.813}$.

$$e^{-9.8135} = 0.00005470803,$$
$$e^{-9.8125} = 0.00005476277.$$

When we round off the insignificant digits,

$$e^{-9.8125} = 0.000547.$$

Although the argument of the exponential had four significant digits, the exponential has only three significant digits.

Exercise 2.14. Determine the number of significant digits in $\sin(95.5°)$.

2.3 GENERATING APPROXIMATE GRAPHS

A rough graph that represents a function can help us to visualize the behavior of the function. The families of functions that we have listed form a repertoire of functions that you can use to generate approximate graphs of functions that are products of other functions. You can recognize the factors as members of the families and can figure out what a graph of the product of the factors will be like from graphs of the factors.The two most important facts are that if any of the factors vanishes, the product vanishes and that if either factor diverges (becomes infinite) the product diverges.

[4] Donald E. Jones, "Significant Digits in Logarithm Antilogarithm Interconversions," J. Chem. Educ. **49**, 753 (1972).

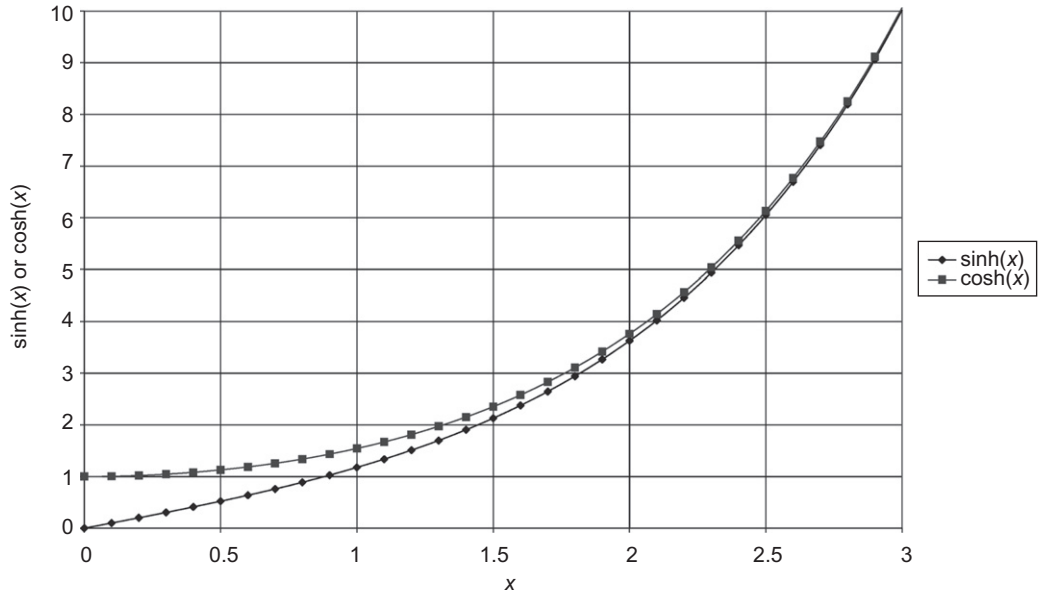


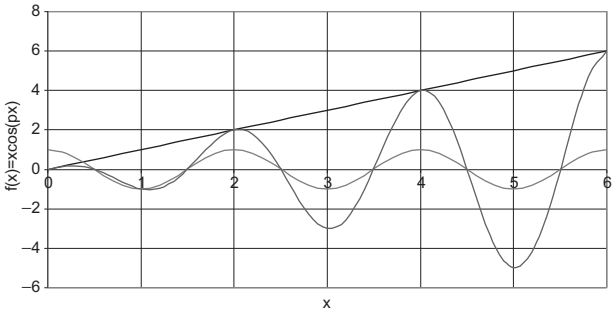
FIGURE 2.10 The hyperbolic sine and cosine.

Example 2.7. Construct a graph of the function

$$y = x\cos(\pi x).$$

Include a graph of each factor in the graph.

This function is a product of the two factors x and $\cos(\pi x)$. The desired rough graph can be constructed by inspection of the graphs of the two factors. The factor x vanishes at the origin and the factor $\cos(x)$ vanishes when $x = \frac{\pi}{2}, \frac{3\pi}{2}$, and so on. Since the cosine oscillates between -1 *and* $+1$, the product oscillates between x and $+x$. A graph showing both factors and their product follows:



Exercise 2.15. Sketch rough graphs of the following functions. Verify your graphs using Excel or Mathematica.

(a) $e^{-x/5}\sin(x)$.
(b) $\sin^2(x) = \left[\sin(x)\right]^2$.

PROBLEMS

1. The following is a set of data for the vapor pressure of ethanol taken by a physical chemistry student. Plot these points by hand on graph paper, with the temperature on the horizontal axis (the *abscissa*) and the vapor pressure on the vertical axis (the *ordinate*). Decide if there are any bad data points. Draw a smooth curve nearly through the points. Use Excel to construct another graph and notice how much work the spreadsheet saves you.

Temperature (°C)	Vapor pressure (torr)
25.00	55.9
30.00	70.0
35.00	97.0
40.00	117.5
45.00	154.1
50.00	190.7
55.00	241.9

2. Using the data from the previous problem, construct a graph of the natural logarithm of the vapor pressure as a function of the reciprocal of the Kelvin temperature. Why might this graph be more useful than the graph in the previous problem?

3. A reactant in a first-order chemical reaction without back reaction has a concentration governed by the same

formula as radioactive decay,

$$[A]_t = [A]_0 e^{-kt},$$

where $[A]_0$ is the concentration at time $t = 0$, $[A]_t$ is the concentration at time t, and k is a function of temperature called the rate constant. If $k = 0.123\ \text{s}^{-1}$ find the time required for the concentration to drop to 21.0% of its initial value.

4. Find the value of the hyperbolic sine, cosine, and tangent for $x = 0$ and $x = \pi/2$. Compare these values with the values of the ordinary (circular) trigonometric functions for the same values of the independent variable.

5. Express the following with the correct number of significant digits. Use the arguments in radians:tan (0.600) sin (0.100)

(a) tan(0.600).
(b) sin(0.100).
(c) cosh(12.0).
(d) sinh(10.0).

6. Sketch rough graphs of the following functions. Verify your graphs using Excel or Mathematica:

(a) $x^2 e^{-x/2}$.
(b) $1/x^2$.
(c) $(1 - x)\, e^{-x}$.
(d) xe^{-x^2}.

7. Tell where each of the following functions is discontinuous. Specify the type of discontinuity:

(a) $\tan(x)$.
(b) $\csc(x)$.
(c) $|x|$.

8. Tell where each of the following functions is discontinuous. Specify the type of discontinuity:

(a) $\cot(x)$.
(b) $\sec(x)$.
(c) $\ln(x - 1)$.

9. If the two ends of a completely flexible chain (one that requires no force to bend it) are suspended at the same height near the surface of the earth, the curve representing the shape of the chain is called a *catenary*. It can be shown[5] that the catenary is represented by

$$y = a \cosh(x/a),$$

where $a = T/g\rho$ and where ρ is the mass per unit length, g is the acceleration due to gravity, and T is the tension force on the chain. The variable x is equal to zero at the center of the chain. Construct a graph of this function such that the distance between the two points of support is 10.0 m, the mass per unit length is 0.500 kg m^{-1}, and the tension force is 100.0 N.

10. For the chain in the previous problem, find the force necessary so that the center of the chain is no more than 0.500 m lower than the ends of the chain.

11. Construct a graph of the two functions: $2\cosh(x)$ and e^x for values of x from 0 to 3. At what minimum value of x do the two functions differ by less than 1%?

12. Verify the trigonometric identity

$$\sin(x + y) = \sin(x)\cos(y) + \cos(x)\sin(y)$$

for the angles $x = 1.0000$ rad, $y = 2.00000$ rad. Use as many digits as your calculator will display and check for round-off error.

13. Verify the trigonometric identity

$$\cos(2x) = 1 - 2\sin^2(x)$$

for $x = 0.50000$ rad. Use as many digits as your calculator will display and check for round-off error.

[5] G.Polya, *Mathematical Methods in Science*, The Mathematical Association of America, 1977, pp. 178ff.

Chapter 3

Problem Solving and Symbolic Mathematics: Algebra

Principal Facts and Ideas

- Algebra is a branch of symbolic mathematics, in which operations are performed symbolically instead of numerically.
- In algebra, the same operations exist as in numerical mathematics.
- The imaginary unit, i, is defined to equal $\sqrt{-1}$.
- A complex number has a real part and an imaginary part that is proportional to i.
- The algebra of complex numbers is an extension of ordinary algebra with its own rules and defined operations.
- Problem solving in chemistry involves organizing the given information, understanding the objective, planning the approach, carrying out the procedures, and checking the answer.

Objectives

After you have studied the chapter, you should be able to:

- Manipulate variables algebraically to simplify algebraic expressions and to obtain more useful equations.
- Perform algebraic operations on complex numbers; form the complex conjugate of any complex number and separate the real and imaginary parts of any complex expression.
- Plan and carry out the solution of typical chemistry problems.

3.1 THE ALGEBRA OF REAL SCALAR VARIABLES

The first branch of symbolic mathematics is algebra. Algebra was invented by Greek mathematicians and developed by Hindu, Arab, and European mathematicians. In symbolic mathematics, letters are used to represent constants and variables, and operations are represented by symbols such as +, −, ×, / or ÷, $\surd$, and so on. Operations are carried out by manipulating these symbols instead of by numerical calculations, so that formulas and equations can be modified and simplified into forms that allow numerical calculations to be carried out later.

The numbers and variables on which we operate in this section are called *real numbers* and *real variables*. They do not include imaginary numbers such as the square root of −1, which we discuss later. They are also called *scalars*, to distinguish them from *vectors*, which have direction as well as magnitude, which we discuss in the next chapter. Real scalar numbers have *magnitude*, a specification of the size of the number, and *sign*, which can be positive or negative. The principal uses of algebra are:

- to simplify an expression,
- to solve an algebraic equation,
- to manipulate an equation or an expression into one that allows numerical calculations to be done more easily.

While operating on an equation, the most important fact is that if you operate on one side of an equation by anything that changes its value, the same operation must be applied to

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00003-3

the other side of the equation. Operations that do not change the value of an expression, such as factoring an expression, multiplying out factors, multiplying the numerator and denominator of a fraction by the same factor, canceling the same factor in a numerator and denominator, can be applied to one side of an equation without destroying its validity.

Example 3.1. Write the following expression in a simpler form:

$$A = \frac{(2x+5)(x+3) - 2x(x+5) - 14}{x^2 + 2x + 1}.$$

We multiply out the factors in the numerator and combine terms, factor the denominator, and cancel a common factor:

$$\begin{aligned} A &= \frac{2x^2 + 11x + 15 - 2x^2 - 10x - 14}{(x+1)(x+1)} \\ &= \frac{x+1}{(x+1)(x+1)} = \frac{1}{x+1}. \end{aligned}$$

Exercise 3.1. Write the following expression in a simpler form:

$$B = \frac{(x^2 + 2x)^2 - x^2(x-2)^2 + 12x^4}{6x^3 + 12x^4}.$$

Example 3.2. The van der Waals equation of state provides a more nearly exact description of real gases than does the ideal gas equation. It is

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT,$$

where P is the pressure, V is the volume, n is the amount of gas in moles, T is the absolute (Kelvin) temperature, and R is the ideal gas constant, equal to 8.314510 J mol^{-1} or 0.08206 l atm K^{-1} mol^{-1}. The quantities a and b are *parameters*, which mean that they are constants that have different values for different gases. Manipulate the van der Waals equation so that the molar volume V_m, defined as V/n, occurs instead of V and n occurring separately. The molar volume is an example of an *intensive variable*, which means that it is independent of the size of the system.

We divide both sides of the equation by n, obtaining

$$\left(P + \frac{n^2 a}{V^2}\right)\left(\frac{V}{n} - b\right) = RT.$$

The equation now contains n and V only as the quotient V/n, so we can write

$$\left(P + \frac{a}{V_\text{m}^2}\right)(V_\text{m} - b) = RT.$$

Exercise 3.2. Manipulate the van der Waals equation into an equation giving P as a function of T and V_m.

3.2 COORDINATE SYSTEMS IN TWO DIMENSIONS

Many of the functions found in physical chemistry depend on position in ordinary space. If an object can move only on a flat surface, we represent this physical surface by a mathematical plane, which is a map of the surface. We choose some point as an origin and pick some line passing through the origin as our x axis. One end of this axis is designated as the positive end. The line passing through the origin perpendicular to the x axis is our y axis, and the positive end of the y axis is counterclockwise 90° from the positive end of the x axis. These axes are shown in Figure 3.1. The origin is labeled as O, and the location of some object is labeled as point P. The x-y plane is divided into four quadrants by the x- and y-axes. The region in which both x and y are positive is the first quadrant and the others are numbered counterclockwise around the plane.

If we draw line segments from the location of the point P perpendicularly to the coordinate axes, we obtain values of x and y. These values are the *Cartesian coordinates* of the point P.[1] We frequently list these values inside parentheses, as in (x, y). Another way to specify the location of the point P is to specify the distance from the origin, denoted by ρ (Greek letter rho), and the value of the angle ϕ (Greek letter phi) between the positive end of the x axis and the line segment from the origin to the point P, measured counterclockwise from the axis. The variables ρ and ϕ are called the *plane polar coordinates* of the point P. If we allow ρ to range from zero to ∞ and allow ϕ to range from 0 to 2π radians (2π rad = 360°), we can specify the location of any point in the plane. Figure 3.1 depicts the two-dimensional Cartesian and polar coordinates of a point.

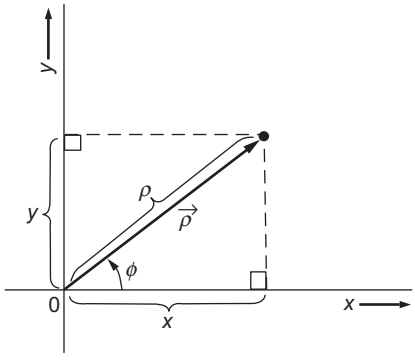


FIGURE 3.1 A mathematical plane, with cartesian and polar coordinates.

[1] Rene du Perron Descartes, 1596–1650, was a French philosopher who spent much of his life in Holland. He was originally trained as a lawyer, but made important contributions in philosophy and mathematics. He is famous for his saying "*Cogito ergo sum*" (I think, therefore I am).

Changing from plane polar coordinates to Cartesian coordinates is an example of *transformation of coordinates* and can be done by using the equations

$$x = \rho\cos(\phi), \tag{3.1}$$
$$y = \rho\sin(\phi). \tag{3.2}$$

The coordinate transformation in the other direction uses the theorem of Pythagoras,[2] Eq. (2.32),

$$\rho = \sqrt{x^2 + y^2}. \tag{3.3}$$

From the definition of the tangent function,

$$\phi = \arctan\left(\frac{y}{x}\right) = \tan^{-1}\left(\frac{y}{x}\right). \tag{3.4}$$

However, since we want ϕ to range from 0 to 2π radians, we must specify this range for the inverse tangent function, instead of using the principal value. If we are using a calculator that is programmed to deliver the principal value, we must decide in advance which quadrant ϕ lies in and be prepared to add π or subtract π to the calculator result if it lies in the wrong quadrant.

Exercise 3.3.

(a) Find x and y if $\rho = 6.00$ and $\phi = \pi/6$ rad.
(b) Find ρ and ϕ if $x = 5.00$ and $y = 10.00$.

3.3 COORDINATE SYSTEMS IN THREE DIMENSIONS

In three dimensions, we will use three coordinate systems: Cartesian coordinates, spherical polar coordinates, and cylindrical polar coordinates.

3.3.1 Cartesian Coordinates

Figure 3.2 depicts the three-dimensional version of *Cartesian coordinates*. We define the x and y axes as before, and erect the z axis through the origin and perpendicular to the x and y axes. We will use a *right-handed coordinate system* like that of Figure 3.1. For this case, if the thumb of the right hand points in the direction of the positive x axis and the index finger points in the direction of the positive y axis, the middle finger can point in the direction of the positive z axis. If the left hand must be used for such an alignment, the coordinate system is called a *left-handed coordinate system.*

[2] Pythagoras of Samos (ca. 570 BC–495 BC) was a famous Greek philosopher and mathematician.

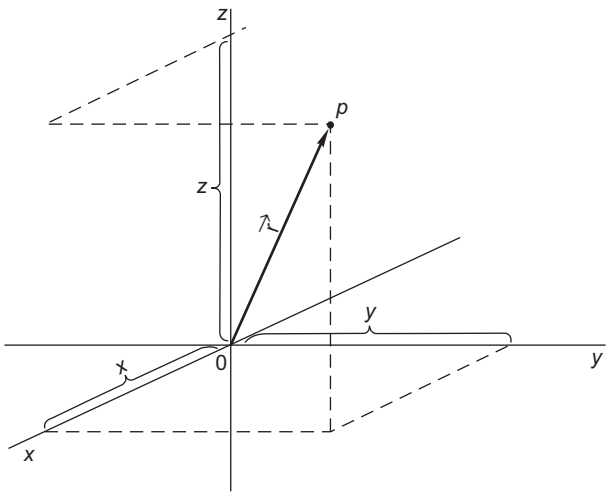


FIGURE 3.2 Cartesian coordinates in three dimensions.

The location of a point P is specified by x, y, and z, which are the *Cartesian coordinates* of the point. These are the distances from the origin to the points on the axes reached by moving perpendicularly from P to each axis. The point P can be denoted by its coordinates, as (x, y, z). The three-dimensional space is divided into eight octants by the coordinate planes. The axes in Figure 2.9 are viewed from the *first octant*, the region in which x, y, and z are all positive. The octants are numbered from 1 to 8, beginning with the first octant in the upper front right part of the coordinate system, moving counterclockwise around the upper part, then numbering the lower front right octant as octant 5 and then moving counterclockwise around the bottom part.

3.3.2 Spherical Polar Coordinates

Figure 3.3 shows the *spherical polar coordinates* that can be used to specify the location of the point P. The directed line segment from the origin to P is denoted by $\mathbf{r}$. The directed line segment ρ in the x-y plane is also shown. The end of this line segment is reached by moving perpendicularly to the x-y plane from the point P. This point is called the *projection* of the point P into the x-y plane. The three spherical polar coordinates are r, θ, and ϕ. The coordinate r is the distance from the origin to the point P, the coordinate θ is the angle between the positive z axis and the directed line segment $\mathbf{r}$, and ϕ is the angle between the positive x axis and directed line segment $\boldsymbol{\rho}$, as in two-dimensional polar coordinates.

The angle θ is allowed to range from 0 to π (0 to 180°) and the angle ϕ is allowed to range from 0 to 2π (0 to 360°). The distance r is allowed to range from 0 to ∞, and these ranges allow the location of any point in the three-dimensional space to be specified.

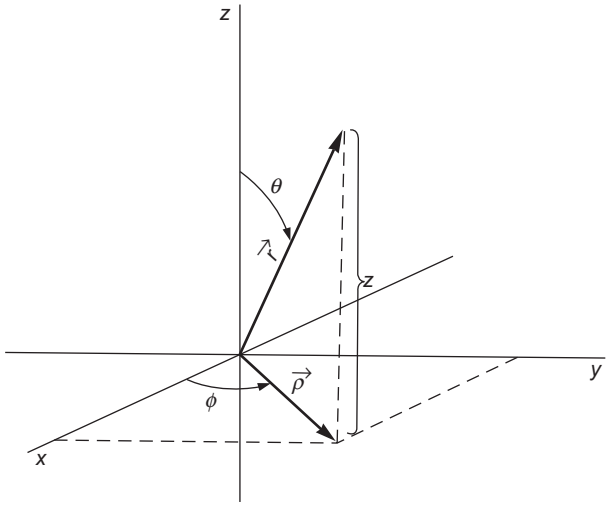


FIGURE 3.3 Spherical polar coordinates.

The following equations can be used to transform from Cartesian coordinates to spherical polar coordinates:

$$\boxed{r = \sqrt{x^2 + y^2 + z^2}}, \tag{3.5}$$

$$\boxed{\theta = \arccos\left(\tfrac{z}{r}\right) = \cos^{-1}\left(\tfrac{z}{r}\right)}, \tag{3.6}$$

$$\boxed{\phi = \arctan\left(\tfrac{y}{x}\right) = \tan^{-1}\left(\tfrac{y}{x}\right)}. \tag{3.7}$$

Equation (3.7) is the same as in plane polar coordinates. Since θ must lie between 0 and π and since ϕ must lie between 0 and 2π be prepared to make sure that your result is in the correct range. Your calculator will presumably display the principal value of the inverse tangent, which is a negative angle for a negative argument. For example, if $x = 4.00$ and $y = -5.00$, the angle ϕ lies in the second quadrant. Your calculator will probably display $-51.34°$ for the inverse tangent. To get the correct value of ϕ, we add 180° to obtain the correct value of ϕ, equal to 128.66°.

The following equations can be used to transform from spherical polar coordinates to Cartesian coordinates:

$$\boxed{x = r\sin(\theta)\cos(\phi)}, \tag{3.8}$$

$$\boxed{y = r\sin(\theta)\sin(\phi)}, \tag{3.9}$$

$$\boxed{z = r\cos(\theta)}. \tag{3.10}$$

Example 3.3. Find the spherical polar coordinates of the point whose Cartesian coordinates are (1.000, 1.000, 1.000).

$$\begin{aligned} r &= \sqrt{(1.000)^2 + \left(1.000\right)^2 + \left(1.000\right)^2} \\ &= \sqrt{3.000} = 1.732, \\ \phi &= \arctan\left(\frac{1.000}{1.000}\right) = \frac{\pi}{4}\text{rad} = 45°, \\ \theta &= \arccos\left(\frac{1.000}{1.732}\right) = 0.955\text{rad} = 54.7°. \end{aligned}$$

Exercise 3.4. Find the spherical polar coordinates of the point whose Cartesian coordinates are (2.00, 3.00, 4.00).

3.3.3 Cylindrical Polar Coordinates

The *cylindrical polar coordinate system* uses the variables ρ and ϕ, which are the same as in two dimensions and are shown in Figure 3.3. The third coordinate, z, is the same as in Cartesian coordinates. The equations needed to transform from Cartesian coordinates to cylindrical polar coordinates are Eqs. (3.3) and (3.4). Equations (3.1) and (3.2) are used for the reverse transformation.

Example 3.4. Find the cylindrical polar coordinates of the point whose Cartesian coordinates are (1.000, −4.000, −2.000).

$$\begin{aligned} \rho &= \sqrt{\left(1.000\right)^2 + \left(4.000\right)^2} = \sqrt{17.000} = 4.123, \\ \phi &= \arctan\left(\frac{-4.000}{1.000}\right) = 4.957 \text{ rad} = 284°, \\ z &= -2.000. \end{aligned}$$

Exercise 3.5. Find the Cartesian coordinates of the point whose cylindrical polar coordinates are $\rho = 25.00$, $\phi = 60.0°$, $z = 17.50$

Exercise 3.6. Find the cylindrical polar coordinates of the point whose Cartesian coordinates are (−2.000, −2.000, 3.000).

The magnitude of the position vector in cylindrical polar coordinates is given by the theorem of Pythagoras

$$r = \left(\rho^2 + z^2\right)^{1/2}. \tag{3.11}$$

Example 3.5. Find the spherical polar coordinates of the points whose cylindrical polar coordinates are $\rho = 10.00$, $\phi = 45.00° = 0.7854$ rad, $z = 15.00$.

$$\begin{aligned} r &= \sqrt{10.00^2 + 15.00^2} = \sqrt{325.00} = 18.03, \\ \theta &= \arccos\left(\frac{15.00}{18.03}\right) = \arccos(0.83205), \\ &= 33.69° = 0.5880 \text{ rad}, \\ \phi &= 45.00° = 0.7854 \text{ rad}. \end{aligned}$$

Exercise 3.7. Find the cylindrical polar coordinates of the point whose spherical polar coordinates are $r = 3.00$, $\theta = 30.00°$, $\phi = 45.00°$.

3.4 IMAGINARY AND COMPLEX NUMBERS

If we confine ourselves to real numbers, there is no such thing as the square root of a negative number. Mathematicians have invented imaginary numbers to make up for this perceived deficiency. The *imaginary unit* is denoted by i and is defined to equal the square root of negative unity:

$$\boxed{i = \sqrt{-1}}\,. \tag{3.12}$$

If b is a real number, the quantity ib is said to be *pure imaginary*, and if a is also real, the quantity

$$c = a + ib \tag{3.13}$$

is said to be a *complex number*. The real number a is called the *real part* of c and is denoted by

$$a = R(c). \tag{3.14}$$

The real number b is called the *imaginary part* of c and is denoted by

$$b = I(c). \tag{3.15}$$

Imaginary and complex numbers cannot be used to represent any physically measurable quantity, but are useful in quantum mechanics, since wave functions can be imaginary or complex.

3.4.1 Mathematical Operations with Complex Numbers

The sum of two complex numbers is obtained by adding the two real parts together and adding the two imaginary parts together. If $c_1 = a_1 + ib_1$ and $c_2 = a_2 + ib_2$, then

$$c_1 + c_2 = a_1 + a_2 + i(b_1 + b_2). \tag{3.16}$$

The product of two complex numbers is obtained by the same procedure as multiplying two real binomials.

$$\begin{aligned} c_1c_2 &= a_1a_2 + i(a_1b_2 + b_1a_2) + \left(i^2\right)b_1b_2, \\ &= a_1a_2 + i(a_1b_2 + b_1a_2) - b_1b_2. \end{aligned} \tag{3.17}$$

As with real numbers, addition and multiplication are *associative*. That is, if a, b, and c are complex numbers,

$$\begin{aligned} a + (b + c) &= (a + b) + c, \\ a(bc) &= (ab)c. \end{aligned} \tag{3.18}$$

Addition and multiplication are *distributive*. That is,

$$a(b + c) = ab + ac. \tag{3.19}$$

Addition and multiplication are *commutative*. That is, addition or multiplication of two complex numbers yields the same result in either order:

$$a + b = b + a, \tag{3.20}$$

$$ab = ba \tag{3.21}$$

Subtraction is the addition of a number whose real and imaginary parts are the negatives of the number to be subtracted. If $c_1 = a_1 + ib_1$ and $c_2 = a_2 + ib_2$ then

$$c_1 - c_2 = a_1 - a_2 + (b_1 - b_2). \tag{3.22}$$

Division by a complex number is more complicated than by a real number. We accomplish division by multiplying by the reciprocal of the number. If

$$z = x + iy,$$

then the *reciprocal* of z, called z^{-1}, is given by

$$\boxed{z^{-1} = \frac{x - iy}{x^2 + y^2}}\,. \tag{3.23}$$

Example 3.6. Show that $z(z^{-1}) = 1$.

$$\begin{aligned} z(z^{-1}) &= (x + iy)\left(\frac{x - iy}{x^2 + y^2}\right), \\ &= \frac{x^2 + ixy - ixy - i^2y^2}{x^2 + y^2} = \frac{x^2 - i^2y^2}{x^2 + y^2} \\ &= \frac{x^2 + y^2}{x^2 + y^2} = 1. \end{aligned}$$

Example 3.7. Show that

$$\frac{a + ib}{c + id} = \frac{ac + bd - iad + ibc}{c^2 + d^2}.$$

$$\begin{aligned} \frac{1}{c + id} &= \frac{c - id}{c^2 + d^2}, \\ \left(\frac{c - id}{c^2 + d^2}\right)(a + ib) &= \frac{ac + bd - iad + ibc}{c^2 + d^2}. \end{aligned}$$

Exercise 3.8. Simplify the expression

$$(4 + 6i)(3 + 2i) + 4i.$$

3.4.2 The Argand Diagram

Specifying a complex number is equivalent to specifying one real number for the real part and one for the imaginary part. We can represent a complex number by the location of a point in a plane, as shown in Figure 3.4. The horizontal coordinate represents the real part of the number and the vertical coordinate represents the imaginary part. The horizontal axis, labeled R, is called the *real axis*, and the vertical axis, labeled I, is called the *imaginary axis*.

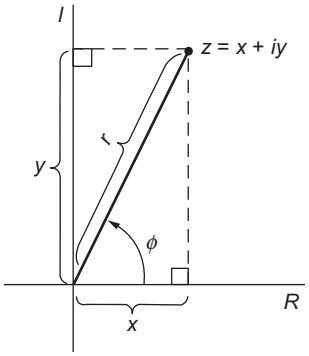


FIGURE 3.4 Representation of the complex number $z = x + iy$ in the argand diagram.

This figure is called the *Argand diagram*, and the plane of the figure is called the *Argand plane* or the *complex plane*. The location of the point in the Argand plane can also be specified using polar coordinates. We use the symbol r for the distance from the origin to the point, and the symbol ϕ for the angle in radians between the positive real axis and the line segment from the origin to the point. The quantity r is the *magnitude* of the complex number and is a nonnegative scalar quantity. It is also called the *absolute value* or the *modulus* of the complex number. The angle ϕ is called the *argument* or *phase* of the complex number. There is a theorem, known as *Euler's formula*[3], that allows a complex number to be written as the product of the magnitude and an exponential with an imaginary exponent,

$$\boxed{z = x + iy = re^{i\phi}}, \tag{3.24}$$

where e is the base of natural logarithms, $e = 2.7182818\cdots$, and where r and ϕ are the magnitude and phase of the complex number. This form is called the *polar representation* of the complex number. In this formula, ϕ must be measured in radians. Inspection of this equation reveals that

$$\boxed{x = r\cos(\phi)}, \tag{3.25}$$

$$\boxed{y = r\sin(\phi)}, \tag{3.26}$$

$$\boxed{r = \sqrt{x^2 + y^2}}, \tag{3.27}$$

$$\boxed{\phi = \arctan(y/x)}. \tag{3.28}$$

In the polar representation, the product of two complex numbers, $z_1 = r_1 e^{i\phi_1}$ and $z_2 = r_2 e^{i\phi_2}$, is given by

$$\boxed{z_1 z_2 = r_1 r_2 e^{i(\phi_1+\phi_2)}}. \tag{3.29}$$

[3] Leonhard Euler (1707–1783) was a great Swiss mathematician whom we have already mentioned.

The quotient $\frac{z_1}{z_2}$ is given by

$$\boxed{\frac{z_1}{z_2} = \frac{r_1 e^{i\phi_1}}{r_2 e^{i\phi_2}} = \left(\frac{r_1}{r_2}\right) e^{i(\phi_1-\phi_2)}}. \tag{3.30}$$

De Moivre's formula gives the result of raising a complex number to a given power:

$$\boxed{\left(r e^{i\phi}\right)^n = r^n e^{in\phi} = r^n[\cos(n\phi) + i\sin(n\phi)]}, \tag{3.31}$$

where n is an integer. Since an angle is unchanged if any multiple of 2π is added or subtracted from it, we can write

$$e^{i(\phi+2n\pi)} = e^{i\phi} \tag{3.32}$$

and

$$\boxed{e^{2\pi i} = 1}. \tag{3.33}$$

Similarly,

$$\boxed{e^{\pi i} = -1}. \tag{3.34}$$

Example 3.8. Evaluate the following:

(a) $(4e^{i\pi})(3e^{2i\pi})$

$$(4e^{i\pi})(3e^{2i\pi}) = 12e^{3i\pi} = 12e^{i\pi}.$$

(b) $(8e^{2i\pi})(2e^{i\pi/2})$

$$(8e^{2i\pi})(2e^{i\pi/2}) = 4e^{5i\pi/2}.$$

(c) $\left(8e^{4i}\right)^2$

$$\left(8e^{4i}\right)^2 = 64e^{8i}.$$

If a number is given in the form $z = x + iy$, we can find the magnitude and the phase as

$$r = \sqrt{x^2 + y^2}, \tag{3.35}$$

$$\phi = \arctan\left(\frac{y}{x}\right) = \tan^{-1}\left(\frac{y}{x}\right). \tag{3.36}$$

Just as with a transformation from Cartesian coordinates to polar coordinates, we must obtain an angle in the proper quadrant, with ϕ ranging from 0 to 2π.

Exercise 3.9. Express the following complex numbers in the form $r\,e^{i\phi}$:

(a) $4.00 + 4.00i$.
(b) -1.00.

Exercise 3.10. Express the following complex numbers in the form $x + iy$:

(a) $z = e^{3\pi i/2}$.
(b) $z = 3e^{\pi i/2}$.

3.4.3 The Complex Conjugate

The *complex conjugate* of a complex number is defined as the number that has the same real part and an imaginary part that is the negative of that of the original number. We will denote the complex conjugate by an asterisk (∗). It is also denoted by a bar over the letter for the number:

If $z = x + iy$, then

$$\boxed{z^* = \bar{z} = \left(x + iy\right)^* = x - iy}. \tag{3.37}$$

Figure 3.5 shows the location of a complex number and of its complex conjugate in the Argand plane.

The phase of the complex conjugate is $-\phi$ if the phase of the original number is ϕ. The magnitude is the same, so

$$\boxed{\left(re^{i\phi}\right)^* = re^{-i\phi}}. \tag{3.38}$$

Although we do not prove it, this equation is an example of a useful fact: *The complex conjugate of any expression is obtained by changing the sign in front of everyithat occurs in the expression.*

Example 3.9. Find the complex conjugates of the following, where a, b, c, and d are real constants:

(a) $A = (1 + 2i)^{3/2} - \exp(3 + 4i)$

$$A^* = (1-2i)^{3/2} - \exp(3-4i) = (1-2i)^{3/2} - e^3 e^{-4i}.$$

(b) $B = a(b + ci)^2 + 4(c - id)^{-1}$

$$B^* = a(b + ci)^2 + 4(c + id)^{-1}.$$

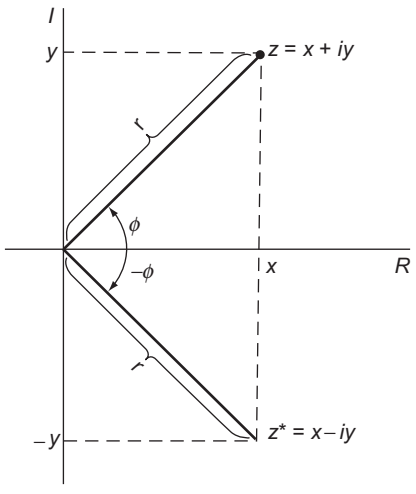


FIGURE 3.5 A complex number, $z = x + iy$ and its complex conjugate, $z = x - iy$ in the argand plane.

Exercise 3.11. Find the complex conjugates of

(a) $A = (x + iy)^2 - 4e^{ixy}$.
(b) $B = (3 + 7i)^3 - (7i)^2$.

Once we have an expression for the complex conjugate of a quantity, we can use it to express the real and imaginary parts separately:

$$R(z) = \frac{1}{2}\left(z + z^*\right) = \frac{1}{2}\left(x + iy + x - iy\right) = x, \tag{3.39}$$

$$I(z) = \frac{1}{2i}\left(z - z^*\right) = \frac{1}{2i}\left(x + iy - x + iy\right) = y. \tag{3.40}$$

3.4.4 The Magnitude of a Complex Quantity

The square of the magnitude of a complex quantity is given by

$$\boxed{|z|^2 = zz^* = \left(r\, e^{i\phi}\right)\left(r\, e^{-i\phi}\right) = r^2}, \tag{3.41}$$

so that the magnitude is given by

$$\boxed{r = \sqrt{zz^*}}, \tag{3.42}$$

where the positive square root is to be taken. The product of any complex number and its complex conjugate is always real and nonnegative, so the magnitude is always real and nonnegative.

Exercise 3.12. Write a complex number in the form $x + iy$ and show that the product of the number with its complex conjugate is real and nonnegative.

Example 3.10. If $z = 4e^{3i} + 6i$, find $R(z)$, $I(z)$, r, and ϕ.

$$\begin{aligned}
R(z) &= \frac{z + z^*}{2} = \frac{4e^{3i} + 6i + 4e^{-3i} - 6i}{2}, \\
&= 2(e^{3i} + e^{-3i}) = 4\cos(3) = -3.960, \\
I(z) &= \frac{z - z^*}{2i} = \frac{4e^{3i} + 6i - 4e^{-3i} + 6i}{2i} \\
&= \frac{4(e^{3i} - e^{-3i})}{2i} + 6 = 4\sin(3) + 6, \\
&= 6.5645, \\
r &= (zz^*)^{1/2} = (x^2 + y^2)^{1/2}, \\
&= [(-3.960)^2 + (6.5645)^2]^{1/2} = 7.666, \\
\phi &= \arctan\left(\frac{I}{R}\right) = \arctan\left(\frac{-6.5645}{3.960}\right) \\
&= \arctan(-1.6577), \\
&= -1.02799.
\end{aligned}$$

The principal value of this arctangent is $-58.90°$ (-1.02799 rad). However, since $R(z)$ is negative and $I(z)$ is positive, if we require an angle in the second quadrant.

$$\phi = 180° - 58.90° = 121.10° = 2.114 \text{ rad}.$$

Exercise 3.13. If $z = (3.00 + 2.00i)^2$, find $R(z), I(z), r$, and ϕ.

3.4.5 Roots of a Complex Number

Just as with real numbers, there are two square roots of a complex number. If $z = r\,e^{i\phi}$, one of the square roots is given by

$$\sqrt{r\,e^{i\phi}} = \sqrt{r}\,e^{i\phi/2}. \tag{3.43}$$

The other square root is obtained by realizing that if ϕ is increased by 2π, the same point in the Argand plane is represented. Therefore, the square root of $r\,e^{i(2\pi+\phi)}$ is the other square root of $r\,e^{i\phi}$. Note that if other multiples of 2π are added to ϕ, no new locations in the Argand diagram are obtained.

$$\sqrt{r\,e^{i\phi}} = \sqrt{r\,e^{i(2\pi+\phi)}} = \sqrt{r}\,e^{i(\pi+\phi/2)}. \tag{3.44}$$

Example 3.11. Find the square roots of $3e^{i\pi/2}$.

One square root is, from Eq. (3.43),

$$\sqrt{3e^{i\pi/2}} = \sqrt{3}e^{i\pi/4}.$$

The other square root is, from Eq. (3.44),

$$\sqrt{3}e^{i(\pi+\pi/4)} = \sqrt{3}e^{i5\pi/4}.$$

If a complex number is represented as $x+iy$, it is easier to transform to polar coordinates before taking the square root of the number.

Exercise 3.14. Find the square roots of $x = 4.00+4.00i$. Sketch an Argand diagram and locate the roots on it.

There are three *cube roots of a complex number*. These can be found by looking for the numbers that when cubed yield $r\,e^{i\phi}$, $r\,e^{i(2\pi+\phi)}$, and $r\,e^{i(4\pi+\phi)}$. These numbers are

$$\sqrt[3]{r\,e^{i\phi}} = \sqrt[3]{r}\,e^{i\phi/3}, \sqrt[3]{r}\,e^{i(2\pi+\phi)/3}, \sqrt[3]{r}\,e^{i(4\pi+\phi)/3}.$$

Example 3.12. Find the three cube roots of -1.

In the polar representation, $-1 = e^{i\pi} = e^{3i\pi} = e^{5i\pi}$. The three cube roots are

$$\sqrt[3]{e^{i\pi}} = e^{i\pi/3},\ e^{i\pi},\ e^{5i\pi/3}.$$

Higher roots are defined in the same way as square roots and cube roots.

Exercise 3.15. Find the four fourth roots of -1.

3.5 PROBLEM SOLVING AND SYMBOLIC MATHEMATICS

In a complicated physical chemistry problem you might have to derive your own mathematical formula or find some approximation scheme. The method must be developed for each problem. The following simple example requires algebraic manipulation as well as numerical calculation:

Under ordinary conditions, gases nearly obey the *ideal gas equation* which is

$$PV = nRT,$$

where V is the volume, n is the amount of gas in moles, T is the temperature, P is the pressure, and R is the *ideal gas constant*. Calculate the volume occupied by 1.278 mol of an ideal gas if the pressure is 2.341 atm and the temperature is 298.15 K.

We symbolically divide both sides of the equation by P, obtaining

$$V = \frac{nRT}{P}.$$

We substitute the numerical values into this equation, convert the pressure from atmospheres to pascals by use of the factor-label method, and carry out the numerical operations:

$$\begin{aligned} V &= \frac{(1.278\ \text{mol})(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})}{2.314\ \text{atm}} \\ &\quad \times \left(\frac{1\ \text{atm}}{101325\ \text{Pa}}\right) \\ &= 1.351 \times 10^{-2}\ \text{J Pa}^{-1} \\ &= 1.351 \times 10^{-2}\ \text{J Pa}^{-1} \left(\frac{1\ \text{Pa}}{1\ \text{N m}^{-2}}\right)\left(\frac{1\ \text{N m}}{1\ \text{J}}\right) \\ &= 1.351 \times 10^{-2}\ \text{m}^3. \end{aligned}$$

We give the answer to four significant digits, because both the pressure and the amount of gas are specified to four significant digits. We can make an additional conversion to express the volume in liters:

$$\left(1.351 \times 10^{-2}\ \text{m}^3\right)\left(\frac{1\ \text{l}}{10^{-3}\text{m}^3}\right) = 13.51\text{l}.$$

We know that this solution is in the correct range of values, since one mole of gas at room temperature and one atmosphere pressure occupy about 25 l.

A procedure for solving problems can be summarized as follows:

1. Analyze the given information and the desired answer.
2. Decide what kind of a procedure is needed to process the given information and obtain the desired answer. Determine whether enough information is contained in the given information. If one or more formulas are

needed, find the formulas. In working a complicated problem, it might be useful to map out on a piece of paper how you are going to get from the given information to the desired answer.[4]

3. Find any addition information that is needed.
4. Carry out any necessary symbolic manipulations to obtain a working formula from the formula or formulas that you found. In some problems you might be asked to obtain a formula, and if so this is the end of the solution.
5. Carry out any numerical operations to obtain the desired answer.
6. Look at your answer to see it if is reasonable. Figure out roughly how large the answer should be. For example, if your answer is a molecular diameter, you know that you should get a value of roughly 10^{-10} m. You can also check your answer by substituting it into the original formula.

It is useful to be able to estimate approximate sizes of things.

Example 3.13. Estimate the number of piano tuners in New York City. We estimate the population to be roughly 10 million people, which might amount to 5 million households. Perhaps one household in 10 might have a piano, for 500,000 pianos. A professional pianist might have a piano tuned every month, but most people might let it go for several years. We assume that on the average, each piano is tuned once in 2 years, for 250,000 tunings per year. A professional piano tuner might be able to tune 6 pianos in a day, or about 1200 pianos in a year. The result is that there might be about 200 full-time piano tuners in New York City.

Exercise 3.16. Estimate the number of house painters in Chicago.

PROBLEMS

1. Manipulate the van der Waals equation into a cubic equation in V_{m}. That is, make a polynomial with terms proportional to powers of V_{m} up to V_{m}^3 on one side of the equation.
2. Find the value of the expression

$$\frac{3\left(2+4\right)^2-6\left(7+|-17|\right)^3+\left(\sqrt{37-|-1|}\right)^3}{\left(1+2^2\right)^4-\left(|-7|+6^3\right)^2+\sqrt{12+|-4|}}.$$

3. A Boy Scout finds a tall tree while hiking and wants to estimate its height. He walks away from the tree and finds that when he is 35 m from the tree, he must look upward at an angle of 32° to look at the top of the tree. His eye is 1.40 m from the ground, which is perfectly level. How tall is the tree?
4. The equation $x^2+y^2+z^2=c^2$, where c is a constant, represents a surface in three dimensions. Express the equation in spherical polar coordinates. What is the shape of the surface?
5. Express the equation $y=b$, where b is a constant, in plane polar coordinates.
6. Express the equation $y=mx+b$, where m and b are constants, in plane polar coordinates.
7. Find the values of the plane polar coordinates that correspond to $x=3.00, y=4.00$.
8. Find the values of the Cartesian coordinates that correspond to $r=5.00, \theta=45°, \phi=135°$.
9. A surface is represented in cylindrical polar coordinates by the equation $z=\rho^2$. Describe the shape of the surface.
10. The solutions to the Schrödinger equation for the electron in a hydrogen atom have three quantum numbers associated with them, called n, l, and m, and these solutions are denoted by ψ_{nlm}.

    (a) The ψ_{210} function is given by

$$\psi_{210}=\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\cos\left(\theta\right),$$

    where $a_0=0.529\times10^{-10}$ m is called the *Bohr radius*. Write this function in terms of Cartesian coordinates.

    (b) The ψ_{211} function is given by

$$\psi_{211}=\frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\sin\left(\theta\right)e^{i\phi}.$$

    Write an expression for the magnitude of this complex function.

    (c) The ψ_{211} function is sometimes called ψ_{2p1}. Write expressions for the real and imaginary parts of the function, which are proportional to the related functions. which are called ψ_{2px} and ψ_{2py}.

11. Find the complex conjugate of the quantity $e^{2.00i}+3e^{i\pi}$
12. Find the sum of $4e^{3i}$ and $5e^{2i}$.
13. Find the difference $3e^{\pi i}-2e^{2i}$.
14. Find the three cube roots of $3-2i$.
15. Find the four fourth roots of $3i$.
16. Find the real and imaginary parts of

$$(3.00+i)^3+(6.00+5.00i)^2.$$

    Find z^*.

17. If $z=\left(\dfrac{3+2i}{4+5i}\right)^2$, find $R(z), I(z)$, r, and ϕ.

[4] Some unkind soul has defined a mathematician as a person capable of designing a mathematically precise path from an unwarranted assumption to a foregone conclusion.

18. Obtain the famous formulas

$$\sin(\phi) = \frac{e^{i\phi} - e^{-i\phi}}{2i} = I(e^{i\phi}),$$
$$\cos(\phi) = \frac{e^{i\phi} + e^{-i\phi}}{2} = R(e^{i\phi}).$$

19. Estimate the number of grains of sand on the beaches of the major continents of the earth. Exclude islands and inland bodies of water. You should come up with a number somewhere near Avogadro's number.

20. A gas has a molar volume of 20 l. Estimate the average distance between nearest-neighbor molecules.

21. Estimate the number of blades of grass in a lawn with an area of 1000 m^2.

22. Since in its early history the earth was too hot for liquid water to exist, it has been theorizedthat all of the water on the earth came from collisions of comets with the earth. Assume an average diameter for the head of a comet and assume that it is completely composed of water ice. Estimate the volume of water on the earth and estimate how many comets would have collided with the earth to supply this much water.

Chapter 4

Vectors and Vector Algebra

Principal Facts and Ideas

- A vector is a quantity with magnitude and direction.
- Several important quantities in physical chemistry are vectors.
- Vector algebra is an extension of ordinary algebra with its own rules.

Objectives

After you have studied the chapter, you should be able to:

- Calculate correctly the sum, difference, scalar product, and vector product of two vectors.
- Apply vectors in physical chemistry problems.

4.1 VECTORS IN TWO DIMENSIONS

We now assume that a point is constrained to move only on a two-dimensional surface, which we represent by a mathematical plane (a map of the surface). The position vector has its tail at the origin and its head at the location of the point. We denote it by the bold-face letter $\boldsymbol{\rho}$ and specify it by the x and y Cartesian coordinates of the point:

$$\boldsymbol{\rho} \leftrightarrow (x, y), \tag{4.1}$$

where the double-headed arrow means "is equivalent to." Figure 4.1 depicts a position vector and the coordinates x and y. We call x and y the *Cartesian components* of the position vector.

Other vector quantities such as velocities and forces are not tied to geographical space as are position vectors, but still require two numbers to represent them in two dimensions. For example, the velocity of a particle is the rate of change of its position vector

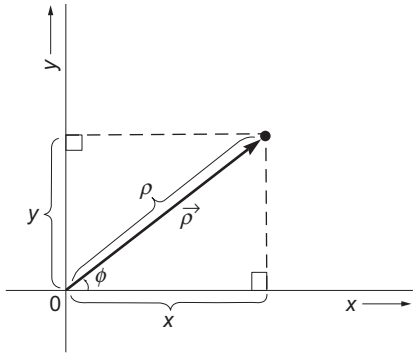


FIGURE 4.1 A position vector in two dimensions.

$$\mathbf{v} = \frac{\mathrm{d}\boldsymbol{\rho}}{\mathrm{d}t}. \tag{4.2}$$

The velocity in two dimensions has two Cartesian components:

$$v_x = \frac{\mathrm{d}x}{\mathrm{d}t}, \tag{4.3}$$

$$v_y = \frac{\mathrm{d}y}{\mathrm{d}t}. \tag{4.4}$$

We define a *velocity space*, which is a mathematical space in which v_x and v_y are plotted on the coordinate axes. We can also define vector spaces for forces, angular momenta, and any other vector quantity.

4.1.1 The Sum and Difference of Two Vectors

We consider a vector to be unchanged if it is moved from one place in a vector space to another, as long as its length

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00004-5

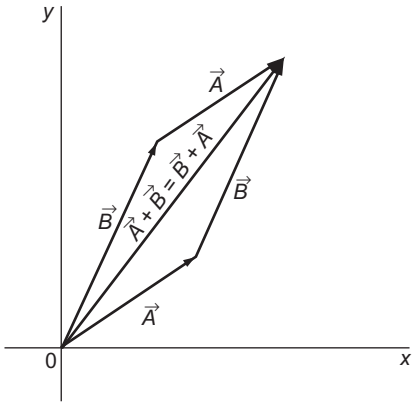


FIGURE 4.2 Two vectors and their sum.

and its direction do not change. The sum of the two vectors can be obtained as follows:

1. Move the second vector without rotating it so that its tail coincides with the head of the first vector.
2. Draw the sum vector from the tail of the first vector to the head of the second.

Figure 4.2 depicts a two-dimensional vector space in which two vectors, **A** and **B**, and their sum are represented. The sum is shown in two ways: one in which vector **A** is moved, and one in which the vector **B** is moved. Vector addition is *commutative*. That is, $\mathbf{A}+\mathbf{B}$ is the same as $\mathbf{B}+\mathbf{A}$, as shown in the figure.

The difference of two vectors is the sum of the first vector and the negative of the second. The negative of a vector is a vector of the same magnitude with the opposite direction. To obtain the vector difference $\mathbf{A}-\mathbf{B}=\mathbf{D}$, the tail of the vector $-\mathbf{B}$ is placed at the head of the vector **A**. The vector $\mathbf{D}=\mathbf{A}-\mathbf{B}$ has its tail at the tail of **A** and its head at the head of $-\mathbf{B}$. The difference $\mathbf{D}=\mathbf{A}-\mathbf{B}$ can also be represented by placing the tails of both **A** and **B** at the same place and drawing the vector **D** with its tail at the head of **B** and its head at the head of **A**. Note that

$$\mathbf{A}-\mathbf{B}=-(\mathbf{B}-\mathbf{A}). \tag{4.5}$$

Exercise 4.1. Draw vector diagrams and convince yourself that the two schemes presented for the construction of $\mathbf{D}=\mathbf{A}-\mathbf{B}$ give the same result.

4.1.2 The Product of a Vector and a Scalar

A general product of a scalar a and a vector **A** is represented by $a\mathbf{A}$. If a is positive, the vector $a\mathbf{A}$ points in the same direction as **A**, and if a is negative, the vector $a\mathbf{A}$ points in the opposite direction. In either case, the magnitude of $a\mathbf{A}$ is equal to $|a||\mathbf{A}|=|a|A$. The product of a scalar and a vector is commutative, so that

$$a\mathbf{A}=\mathbf{A}a. \tag{4.6}$$

4.1.3 Unit Vectors

A more systematic way to represent vectors is with *unit vectors*. We define **i** to be a vector of unit length pointing in the direction of the positive end of the x axis, and **j** to be a vector of unit length pointing in the direction of the positive end of the y axis. The position vector $\boldsymbol{\rho}$ can be represented by the sum of two vector terms

$$\boldsymbol{\rho}=\mathbf{i}x+\mathbf{j}y. \tag{4.7}$$

The term $\mathbf{i}x$ is the product of a scalar, x, and a vector, **i**. If x is positive, $\mathbf{i}x$ is a vector of length x pointing in the direction of **i** (toward the positive end of the x axis). If x is negative, $\mathbf{i}x$ points in the opposite direction. The second term is a vector pointing in the y direction. Any vector in two dimensions can be represented in the same way. We write

$$\mathbf{A}=\mathbf{i}A_x+\mathbf{j}A_y, \tag{4.8}$$

where A_x and A_y are the *components* of **A**. The term $\mathbf{i}A_x$ is a product of the component A_x (a scalar) and a vector **i**, so it is a vector of length A_x pointing along the x axis. If A_x is negative, the term $\mathbf{i}A_x$ points in the direction of the negative end of the x axis. The other term is similarly a vector of length A_y pointing along the y axis. We can also denote the vector **A** by its component in x,y order inside parentheses, as (A_x,A_y).

The sum of $\mathbf{i}A_x$ and $\mathbf{j}A_y$ is represented in Figure 4.3.

The Product of a Scalar and a Vector in Terms of Components

The product $a\mathbf{A}$ is the vector

$$a\left(\mathbf{i}A_x+\mathbf{j}A_y\right)=\mathbf{i}aA_x+\mathbf{j}aA_y. \tag{4.9}$$

The components are

$$(a\mathbf{A})_x=aA_x, \tag{4.10}$$

$$(a\mathbf{A})_y=aA_y. \tag{4.11}$$

The Sum of Two Vectors in Terms of Components

The vector **A** and the vector **B** can be represented as

$$\mathbf{A}=\mathbf{i}A_x+\mathbf{j}A_y, \tag{4.12}$$

$$\mathbf{B}=\mathbf{i}B_x+\mathbf{j}B_y. \tag{4.13}$$

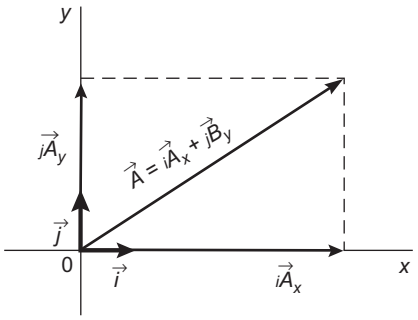


FIGURE 4.3 A vector in terms of the unit vectors **i** and **j**.

If the sum of **A** and **B** is called **C**, we can write

$$\mathbf{C} = \mathbf{i}A_y + \mathbf{j}B_y, \tag{4.14}$$

$$C_x = A_x + B_x, \tag{4.15}$$

$$C_y = A_y + B_y. \tag{4.16}$$

Example 4.1. Find the sum of the two vectors (2.5,3.0) and (3.1,4.0).

$$\mathbf{A} + \mathbf{B} = (5.6,\ 7.0).$$

The difference of two vectors is the sum of the first vector and the negative of the second. If the vector $\mathbf{A} - \mathbf{B} = \mathbf{D}$,

$$D_x = A_x - B_x, \tag{4.17}$$

$$D_y = A_y - B_y. \tag{4.18}$$

Exercise 4.2. Find $\mathbf{A} - \mathbf{B}$ if $\mathbf{A} = (2.50,1.50)$ and $\mathbf{B} = (1.00, -7.50)$.

4.1.4 The Scalar Product of Two Vectors

In two dimensions, there is only one type of product of two vectors. It is called the *scalar product,* since the product is a scalar. It is also called the *dot product* because of the use of a dot to represent the operation. If **A** and **B** are two vectors and α is the angle between them, their scalar product is denoted by $\mathbf{A} \cdot \mathbf{B}$ and defined by

$$\boxed{\mathbf{A} \cdot \mathbf{B} = |\mathbf{A}||\mathbf{B}| \cos(\alpha)} \quad \text{(definition)}, \tag{4.19}$$

where $|\mathbf{A}|$ is the magnitude of **A** and $|\mathbf{B}|$ is the magnitude of **B** and where α is the angle between the vectors, measured so that it is no greater than 180°.

Example 4.2. Let $|\mathbf{A}| = 4.50, |\mathbf{B}| = 6.00$, and let the angle between them equal 30.0°. Find $\mathbf{A} \cdot \mathbf{B}$

$$\begin{aligned}\mathbf{A} \cdot \mathbf{B} &= 4.50 \times 6.00 \times \cos(30°) \\ &= 4.50 \times 6.00 \times 0.86603\cdots = 23.4.\end{aligned}$$

Exercise 4.3. Let $|\mathbf{A}| = 4.00, |\mathbf{B}| = 2.00$, and let the angle between them equal 45.0°. Find $\mathbf{A} \cdot \mathbf{B}$.

The scalar product has the properties:

- If **A** and **B** are parallel, $\mathbf{A} \cdot \mathbf{B}$ is the product of the magnitudes of **A** and **B**.
- If **A** and **B** are antiparallel, $\mathbf{A} \cdot \mathbf{B}$ is the negative of the product of the magnitudes of **A** and **B**.
- If **A** and **B** are perpendicular to each other, $\mathbf{A} \cdot \mathbf{B} = 0$. Such vectors are said to be *orthogonal* to each other.

The scalar product $\mathbf{A} \cdot \mathbf{B}$ can be written in terms of components:

$$\begin{aligned}\mathbf{A} \cdot \mathbf{B} &= \left(\mathbf{i}A_x + \mathbf{j}A_y\right) \cdot \left(\mathbf{i}B_x + \mathbf{j}B_y\right) \\ &= \mathbf{i} \cdot \mathbf{i}A_xB_x + \mathbf{i} \cdot \mathbf{j}A_xB_y + \mathbf{j} \cdot \mathbf{i}A_yB_x \\ &\quad + \mathbf{j} \cdot \mathbf{j}A_yB_y. \end{aligned} \tag{4.20}$$

From the definitions of **i** and **j** and the definition of the scalar product,

$$\mathbf{i} \cdot \mathbf{i} = \mathbf{j} \cdot \mathbf{j} = 1, \tag{4.21}$$

$$\mathbf{i} \cdot \mathbf{j} = \mathbf{j} \cdot \mathbf{i} = 0, \tag{4.22}$$

so that

$$\boxed{\mathbf{A} \cdot \mathbf{B} = A_xB_x + A_yB_y}. \tag{4.23}$$

Example 4.3. If: $\mathbf{A} = 2.50\mathbf{i} + 4.00\mathbf{j}$ and $\mathbf{B} = 3.00\mathbf{i} - 5.00\mathbf{j}$,

(a) Find $A \cdot B$

$$\begin{aligned}A \cdot B &= (2.5)(3.0) + (4.0)(-5.0) \\ &= 7.5 - 20.0 = -12.5.\end{aligned}$$

(b) Find the angle between A and B

$$\begin{aligned}|\mathbf{A}| &= (6.25 + 16)^{1/2} = (22.25)^{1/2} \\ &= 4.717\cdots \approx 4.7, \\ |\mathbf{B}| &= (9.0 + 25)^{1/2} = (34)^{1/2} \\ &= 5.8309\cdots \approx 5.8, \\ \cos(\alpha) &= \frac{\mathbf{A} \cdot \mathbf{B}}{|\mathbf{A}||\mathbf{B}|} = \frac{-12.5}{(4.717)(5.831)} \\ &= -0.4545 \approx -0.454, \\ \alpha &= \arccos\left(-0.4545\right) = 2.04 \text{ rad} = 117°.\end{aligned}$$

Exercise 4.4. If $\mathbf{A} = (3.00)\mathbf{i} - (4.00)\mathbf{j}$ and $\mathbf{B} = (1.00)\mathbf{i} + (2.00)\mathbf{j}$.

(a) Draw a vector diagram of the two vectors.
(b) Find $A \cdot B$ and $(2A) \cdot (3B)$.

4.1.5 The Magnitude of a Vector

The magnitude of a vector **A** is denoted by A or by $|\mathbf{A}|$. The scalar product of a vector with itself gives the square of the magnitude of the vector:

$$(\mathbf{A} \cdot \mathbf{A}) = |\mathbf{A}|^2 = (A_x^2 + A_y^2), \tag{4.24}$$

$$|\mathbf{A}| = (A_x^2 + A_y^2)^{1/2}. \tag{4.25}$$

.

Example 4.4. The vector **A** has the components $A_x = 2.00, A_y = 3.00$. The vector **B** has the components $B_x = 3.00, B_y = 4.00$.

(a) Find $|\mathbf{A}|$ and $|\mathbf{B}|$

$$\begin{aligned} |\mathbf{A}| &= A = \left[(2.00)^2 + (3.00)^2\right]^{1/2} \\ &= \sqrt{13.00} = 3.61, \\ |\mathbf{B}| &= B = \left[(3.00)^2 + (4.00)^2\right]^{1/2} \\ &= \sqrt{25.00} = 5.00. \end{aligned}$$

(b) Find the components and the magnitude of $A + B$. Let $A + B = C$

$$\begin{aligned} C_x &= 5.00, C_y = 7.00, \\ C &= \left[(5.00)^2 + (7.00)^2\right]^{1/2} \\ &= \sqrt{74.00} = 8.60. \end{aligned}$$

(c) Find $A \cdot B$

$$A \cdot B = (2.00)(3.00) + (3.0)(4.00) = 18.00 = 18.00.$$

(d) Find the angle between A and B

$$\begin{aligned} \cos(\alpha) &= \frac{18.00}{(3.61)(5.00)} = 0.99846, \\ \alpha &= \arccos(0.99846) = 3.18^\circ = 0.0555 \text{ rad}. \end{aligned}$$

Exercise 4.5. If $\mathbf{A} = 2.00\mathbf{i} - 3.00\mathbf{j}$ and $\mathbf{B} = -1.00\mathbf{i} + 4.00\mathbf{j}$

(a) Find $|\mathbf{A}|$ and $|\mathbf{B}|$.
(b) Find the components and the magnitude of $2.00\mathbf{A} - \mathbf{B}$.
(c) Find $\mathbf{A} \cdot \mathbf{B}$.
(d) Find the angle between A and B.

4.2 VECTORS IN THREE DIMENSIONS

4.2.1 Unit Vectors in Three Dimensions

For vectors in three dimensions, we introduce the unit vector **k**, which points in the direction of the positive end of the z axis, in addition to the unit vectors **i** and **j** in the x and y directions. Figure 4.4 shows the unit vectors and the position vector **r**, which can be represented as the vector sum

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z. \tag{4.26}$$

An arbitrary vector **A** is represented by the vector sum

$$\mathbf{A} = \mathbf{i}A_x + \mathbf{j}A_y + \mathbf{k}A_z, \tag{4.27}$$

where we have three *Cartesian components*, A_x, Ay, and A_z. The vector can be represented by (A_x, A_y, A_z).

4.2.2 The Magnitude of a Vector

The magnitude of the position vector **r** is denoted $|\mathbf{r}|$ or by r. In Figure 4.4 you can see that r is the hypotenuse of a right triangle with sides ρ and z, where $\rho = \sqrt{x^2 + y^2}$ so that the square of the magnitude of **r** is given by the theorem of Pythagoras:

$$\boxed{r^2 = \rho^2 + z^2 = x^2 + y^2 + z^2} \tag{4.28}$$

or

$$\boxed{r = |\mathbf{r}| = \sqrt{x^2 + y^2 + z^2}}. \tag{4.29}$$

If **A** is a vector with Cartesian components A_x, A_y, and A_z, the magnitude of **A** is given by

$$\boxed{|\mathbf{A}| = A = \left(A_x^2 + A_y^2 + A_z^2\right)^{1/2} = \sqrt{A_x^2 + A_y^2 + A_z^2}}. \tag{4.30}$$

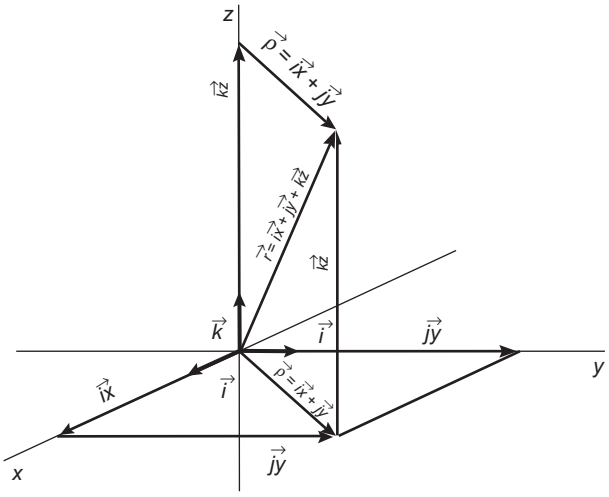


FIGURE 4.4 A position vector in terms of the unit vectors **i**, **j**, and **k**.

Example 4.5. Find the magnitude of the vector $\mathbf{A} = (3.00, 4.00, 5.00)$

$$|\mathbf{A}| = A = \sqrt{3.00^2 + 4.00^2 + 5.00^2} = \sqrt{50.00} = 7.071$$

Exercise 4.6. Find the magnitude of the vector $\mathbf{A} = (-3.00, 4.00, -5.00)$.

4.2.3 The Sum and Difference of Two Vectors

The sum of two vectors in three dimensions is analogous to the sum in two dimensions. Let **A** and **B** be two vectors, represented in terms of their components by

$$\mathbf{A} = \mathbf{i}A_x + \mathbf{j}A_y + \mathbf{k}A_z, \tag{4.31}$$
$$\mathbf{B} = \mathbf{i}B_x + \mathbf{j}B_y + \mathbf{k}B_z. \tag{4.32}$$

As in two dimensions the sum is obtained by placing the tail of the second vector at the head of the first without rotating it and then drawing the sum vector from the tail of the first to the head of the second. We can more easily work with the components. If **C** is the sum of **A** and **B**, then

$$\mathbf{C} = \mathbf{i}(A_\mathbf{x} + B_\mathbf{x}) + j(A_\mathbf{y} + B_\mathbf{y}) + k(A_\mathbf{z} + B_z), \tag{4.33}$$
$$C_x = A_x + B_x, \tag{4.34}$$
$$C_y = A_y + B_y, \tag{4.35}$$
$$C_z = A_z + B_z. \tag{4.36}$$

The difference $\mathbf{A} - \mathbf{B}$ is the sum of **A** and the negative of **B**

$$\mathbf{A} - \mathbf{B} = \mathbf{D} = \mathbf{i}(A_x - B_x) + \mathbf{j}(A_y - B_y) + \mathbf{k}(A_z - B_z). \tag{4.37}$$

4.2.4 The Product of a Scalar and a Vector

The product of a three-dimensional vector **A** and a scalar a is also analogous to the product in two dimensions. If the scalar constant a is positive, the product $a\mathbf{A}$ is a vector in the same direction as **A** with magnitude equal to a times $|\mathbf{A}|$. If a is negative, the direction of $a\mathbf{A}$ is opposite to the direction of **A**

$$\boxed{a\mathbf{A} = \mathbf{i}aA_x + \mathbf{j}aA_y + \mathbf{k}aA_z}. \tag{4.38}$$

$$|a\mathbf{A}| = |a||\mathbf{A}| = |a|A. \tag{4.39}$$

4.2.5 The Scalar Product of Two Vectors

Just as in two dimensions the scalar product of two vectors is given by the product of the magnitudes of the vectors and the cosine of the angle between them:

$$\boxed{\mathbf{A} \cdot \mathbf{B} = |\mathbf{A}||\mathbf{B}| \cos(\alpha) = AB\cos(\alpha)}, \tag{4.40}$$

where α is the angle between the vectors. If two vectors are perpendicular to each other, their scalar product vanishes. Vectors that are perpendicular to each other are sometimes said to be *orthogonal* to each other.

The unit vectors have unit magnitude and are mutually orthogonal to each other

$$\boxed{\mathbf{i} \cdot \mathbf{i} = \mathbf{j} \cdot \mathbf{j} = \mathbf{k} \cdot \mathbf{k} = 1}, \tag{4.41}$$

$$\boxed{\mathbf{i} \cdot \mathbf{j} = \mathbf{j} \cdot \mathbf{k} = \mathbf{k} \cdot \mathbf{i} = 0}. \tag{4.42}$$

Using these relations, we have

$$\boxed{\mathbf{A} \cdot \mathbf{B} = A_x B_x + A_y B_y + A_z B_z}. \tag{4.43}$$

Example 4.6. Let $A = 2\mathbf{i} + 3\mathbf{j} + 7\mathbf{k}$ and $B = 7\mathbf{i} + 2\mathbf{j} + 3\mathbf{k}$.

(a) Find $A \cdot B$ and the angle between A and B

$$\mathbf{A} \cdot \mathbf{B} = 14 + 6 + 21 = 41.$$

The magnitude of A in this example happens to equal the magnitude of B:

$$|\mathbf{A}| = A = |B| = B = (2^2 + 3^2 + 7^2)^{1/2} = \sqrt{62}.$$

Let α be the angle between the vectors A and B

$$\alpha = \arccos\left(\frac{\mathbf{A} \cdot \mathbf{B}}{|\mathbf{A}||\mathbf{B}|}\right) = \arccos\left(\frac{41}{\sqrt{62}\sqrt{62}}\right) = \arccos(0.6613) = 0.848 \text{ rad} = 48.6°.$$

(b) Find $(3A) \cdot B$

$$(3\mathbf{A}) \cdot \mathbf{B} = 6 \times 7 + 9 \times 2 + 21 \times 3 = 123 = 3\mathbf{A} \cdot \mathbf{B}.$$

Exercise 4.7.

(a) Find the Cartesian components of the position vector whose spherical polar coordinates are $r = 2.00$, $\theta = 90°$, $\phi = 0°$. Call this vector A.
(b) Find the scalar product of the vector A from part a and the vector B whose Cartesian components are (1.00,2.00,3.00).
(c) Find the angle between these two vectors.

4.2.6 The Vector Product of Two Vectors

In three dimensions there is second kind of a product between two vectors that does not exist in two dimensions. It is called the *vector product* and denoted by $\mathbf{A} \times \mathbf{B}$. It is also called the *cross product* because of the symbol used. If the vector **C** is the vector product of **A** and **B**,

$$\mathbf{C} = \mathbf{A} \times \mathbf{B}, \tag{4.44}$$

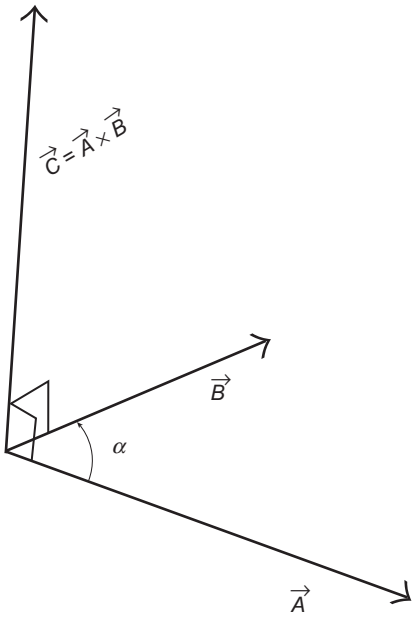


FIGURE 4.5 The vector product of two vectors.

then **C** is defined to have the magnitude

$$|\mathbf{C}| = C = |\mathbf{A}|\,|\mathbf{B}| \sin(\alpha) = AB \sin(\alpha) \quad \text{(definition)}, \tag{4.45}$$

where α is the angle between **A** and **B**, measured so that it lies between 0° and 180°. The cross product **C** is defined to be perpendicular to the plane containing **A** and **B** and its direction is defined as follows: If the first vector listed is rotated through the angle α so that its direction coincides with that of **B**, then **C** points in the direction that an ordinary (right-handed) screw thread would move with this rotation. Another rule to obtain the direction is a *right-hand rule*. If the thumb of the right hand points in the direction of the first vector and the index finger points in the direction of the second vector, the middle finger can point in the direction of their cross product.

Figure 4.5 depicts two vectors and their vector product. The vector product has the properties:

- The cross product operation is not *commutative*, which means that if the order of the two factors is switched, a different result is obtained. The vector product $\mathbf{A} \times \mathbf{B}$ is the negative of the vector product $\mathbf{B} \times \mathbf{A}$.

Exercise 4.8. From the definition, show that

$$\boxed{\mathbf{A} \times \mathbf{B} = -(\mathbf{B} \times \mathbf{A})}.$$

- If **A** and **B** are parallel to each other, their vector product vanishes:

$$\boxed{\mathbf{A} \times \mathbf{B} = \mathbf{0}} \quad (\mathbf{A} \text{ and } \mathbf{B} \text{ parallel}), \tag{4.46}$$

where **0** is the *null vector*. The null vector is defined to have zero magnitude and no particular direction.

- If two vectors are perpendicular to each, the magnitude of their cross product is equal to the product of their magnitudes. since the sine of 90° is equal to unity

$$\boxed{|\mathbf{A} \times \mathbf{B}| = |\mathbf{A}||\mathbf{B}|} \quad (\mathbf{A} \text{ and } \mathbf{B} \text{ perpendicular}). \tag{4.47}$$

To express the cross product in terms of components, we can use the definition of the vector product to write

$$\boxed{\mathbf{i} \times \mathbf{i} = \mathbf{j} \times \mathbf{j} = \mathbf{k} \times \mathbf{k} = 0}, \tag{4.48}$$

$$\boxed{\mathbf{i} \times \mathbf{j} = \mathbf{k}}, \boxed{\mathbf{j} \times \mathbf{i} = -\mathbf{k}},$$

$$\boxed{\mathbf{k} \times \mathbf{i} = \mathbf{j}}, \boxed{\mathbf{i} \times \mathbf{k} = -\mathbf{j}},$$

$$\boxed{\mathbf{k} \times \mathbf{i} = \mathbf{j}}, \boxed{\mathbf{k} \times \mathbf{j} = -\mathbf{i}}.$$

If $\mathbf{C} = \mathbf{A} \times \mathbf{B}$ we find from these relations that

$$\boxed{\begin{aligned}\mathbf{C} = \mathbf{A} \times \mathbf{B} &= \mathbf{i}(A_y B_z - A_z B_y) \\ &+ \mathbf{j}(A_z B_x - A_x B_z) + \mathbf{k}(A_x B_y - A_y B_x)\end{aligned}}. \tag{4.49}$$

The other three possible terms vanish since the cross product of a vector with itself vanishes.

Example 4.7. Find the cross product $\mathbf{A} \times \mathbf{B}$, where $\mathbf{A} = (1.00, 2.00, 3.00)$ and $\mathbf{B} = (1.00, 1.00, 1.00)$

$$\mathbf{C} = \mathbf{A} \times \mathbf{B} = \mathbf{i}(2-3) + \mathbf{j}(3-1) + \mathbf{k}(1-2) = -\mathbf{i} + 2\mathbf{j} - \mathbf{k}.$$

Example 4.8. Show that the vector **C** obtained in the previous example is perpendicular to **A**.

We show that $\mathbf{A} \cdot \mathbf{C} = 0$

$$\begin{aligned}\mathbf{A} \cdot \mathbf{C} &= A_x C_x + A_y C_y + A_z C_z, \\ &= -1 + 4 + 3 = 0.\end{aligned}$$

Exercise 4.9. Show that the vector **C** is perpendicular to **B**.

4.3 PHYSICAL EXAMPLES OF VECTOR PRODUCTS

4.3.1 Magnetic Force

An example of a vector product is the force on a moving charged particle due to a magnetic field. If q is the charge on the particle measured in coulombs C, **v** is the velocity of the particle in meters per second, and **B** is the*magnetic*

induction (often called the "magnetic field") measured in *tesla* (T),[1] the force in Newtons is given by

$$\mathbf{F} = q\mathbf{v} \times \mathbf{B}. \tag{4.50}$$

Since this force is perpendicular to the velocity, it causes the trajectory of the particle to curve, rather than changing the speed of the particle.

Example 4.9. Find the force on an electron in a magnetic field if $\mathbf{v} = \mathbf{i}(1.000 \times 10^5 \text{ m s}^{-1})$ and $\mathbf{B} = \mathbf{j}(5.000 \text{ T})$ (the magnetic field in a large electromagnet).

The value of the charge on an electron is $q = -1.602 \times 10^{-19}$ C (note the negative sign)

$$\begin{aligned}
\mathbf{F} &= (\mathbf{i} \times \mathbf{j})\left(-1.602 \times 10^{-19} \text{ C}\right) \\
&\quad \times \left(1.000 \times 10^5 \text{ m s}^{-1}\right)(5.000 \text{ T}) \\
&= (\mathbf{i} \times \mathbf{j})\left(-1.602 \times 10^{-19} \text{ A s}\right) \\
&\quad \times \left(1.000 \times 10^5 \text{ m s}^{-1}\right)\left(5.000 \text{ kg s}^{-2} \text{ A}^{-1}\right) \\
&= -\mathbf{k}\left(8.011 \times 10^{-14} \text{ A s m s}^{-1} \text{ kg s}^{-2} \text{ A}^{-1}\right) \\
&= -\mathbf{k}\left(8.011 \times 10^{-14} \text{ kg m s}^{-2}\right) \\
&= -\mathbf{k}(8.011 \times 10^{-14} \text{ N}).
\end{aligned}$$

Exercise 4.10. The magnitude of the earth's magnetic field ranges from 0.25 to 0.65 G (gauss). Assume that the average magnitude is equal to 0.45 G, which is equivalent to 0.000045 T. Find the magnitude of the force on the electron in the previous example due to the earth's magnetic field, assuming that the velocity is perpendicular to the magnetic field.

4.3.2 Electrostatic Force

The force on a charged particle due to an *electric field* is given as the product of a scalar and a vector:

$$\mathbf{F} = q\mathbf{E}, \tag{4.51}$$

where $\mathbf{F}$ is the force, $\mathbf{E}$ is the electric field, and q is the charge on the particle. If the charge is measured in coulombs C and the field in volts per meter (V m^{-1}), the force is in Newtons (/N).

Example 4.10. Find the direction and the magnitude of the electric field necessary to provide a force on the electron in the previous example that is equal in magnitude to the force due to the magnetic field but opposite in direction. If both these forces act on the particle, what will be their effect?

[1] The tesla is named for Nikola Tesla, 1856–1943, the electrical engineer who invented the rotating-field electric motor and other electrical devices.

Since the force in the previous example is in the negative z direction, the electrostatic force must be in the positive z direction

$$\begin{aligned}
\mathbf{E} &= \mathbf{k}\left(\frac{F}{q}\right) = \mathbf{k}\left(\frac{8.011 \times 10^{-14} \text{ kg m s}^{-2}}{1.602 \times 10^{-19} \text{ C}}\right) \\
&= \mathbf{k}\left(5.00 \times 10^5 \text{ kg m}^2 \text{ s}^{-2} \text{ C}^{-1} \text{ m}^{-1}\right) \\
&= \mathbf{k}\left(5.00 \times 10^5 \text{ V m}^{-1}\right).
\end{aligned}$$

We have used the equivalence that a joule per coulomb is a volt.

4.3.3 Angular Momentum

If a particle of mass m is moving relative to the origin of coordinates, its angular momentum around the origin is denoted by $\mathbf{L}$ and is given by

$$\mathbf{L} = m\mathbf{r} \times \mathbf{v}, \tag{4.52}$$

where $\mathbf{r}$ is the position vector of the particle and $\mathbf{v}$ is its velocity.

Example 4.11. If a particle has a mass of 1.000×10^{-3} kg and its position and velocity are $r = \mathbf{i}$ (4.00 m) and $v = \mathbf{j}$ (24.00 m s^{-1}), find the angular momentum of the particle

$$\begin{aligned}
\mathbf{L} &= (1.000 \times 10^{-3} \text{ kg})\left(4.00 \text{ m}\right)(24.00 \text{ m s}^{-1})\mathbf{i} \times \mathbf{j} \\
&= \mathbf{k}\ (9.60 \times 10^{-2} \text{ kg m s}^{-1}).
\end{aligned}$$

Exercise 4.11. A boy is swinging a weight around his head on a rope. Assume that the weight has a mass of 0.650 kg, that the rope plus the effective length of the boy's arm has a length of 1.45 m, and that the weight makes a complete circuit in 1.34 s. Find the magnitude of the angular momentum, excluding the mass of the rope and the boy's arm. If the mass is moving counterclockwise in a horizontal circle, what is the direction of the angular momentum?

PROBLEMS

1. Find $\mathbf{A} - \mathbf{B}$ if $\mathbf{A} = 2.00\mathbf{i} + 3.00\mathbf{j}$ and $\mathbf{B} = 1.00\mathbf{i} + 3.00\mathbf{j} - 1.00\mathbf{k}$.
2. An object of mass $m = 10.0$ kg near the surface of the earth has a horizontal force of 98.0 N acting on it in the eastward direction in addition to the gravitational force. Find the vector sum of the two forces (the resultant force).
3. Find $\mathbf{A} \cdot \mathbf{B}$ if $\mathbf{A} = (0,2)$ and $\mathbf{B} = (2,0)$.
4. Find $|\mathbf{A}|$if $\mathbf{A} = 3.00\mathbf{i} + 4.00\mathbf{j} - 5.00\mathbf{k}$.
5. Find $\mathbf{A} \cdot \mathbf{B}$ if $\mathbf{A} = (1.00)\mathbf{i} + (2.00)\mathbf{j} + (3.00\mathbf{k}$ and $\mathbf{B} = (1.00)\mathbf{i} + (3.00)\mathbf{j} - (2.00)\mathbf{k}$.

6. Find $\mathbf{A} \cdot \mathbf{B}$ if $\mathbf{A} = (1.00, 1.00, 1.00)$ and $\mathbf{B} = (2.00, 2.00, 2.00)$.

7. Find $\mathbf{A} \times \mathbf{B}$ if $\mathbf{A} = (0.00, 1.00, 2.00)$ and $\mathbf{B} = (2.00, 1.00, 0.00)$.

8. Find $\mathbf{A} \times \mathbf{B}$ if $\mathbf{A} = (1,1,1)$ and $\mathbf{B} = (2,2,2)$.

9. Find the angle between $\mathbf{A}$ and $\mathbf{B}$ if $\mathbf{A} = 1.00\mathbf{i} + 2.00\mathbf{j} + 1.00\mathbf{k}$ and $\mathbf{B} = 1.00\mathbf{i} - 1.00\mathbf{k}$.

10. Find the angle between $\mathbf{A}$ and $\mathbf{B}$ if $\mathbf{A} = 3.00\mathbf{i} + 2.00\mathbf{j} + 1.00\mathbf{k}$ and $\mathbf{B} = 1.00\mathbf{i} + 2.00\mathbf{j} + 3.00\mathbf{k}$.

11. A spherical object falling in a fluid has three forces acting on it: (1) The gravitational force, whose magnitude is $F_g = mg$, where m is the mass of the object and g is the acceleration due to gravity, equal to 9.80 m s^{-2}; (2) The buoyant force, whose magnitude is $F_b = m_f g$, where m_f is the mass of the displaced fluid, and whose direction is upward; (3) The frictional force, which is given by $\mathbf{F}_f = -6\pi\eta r\mathbf{v}$, where r is the radius of the object, $\mathbf{v}$ is its velocity, and η is the coefficient of viscosity of the fluid. This formula for the frictional forces applies only if the flow around the object is laminar (flow in layers). The object is falling at a constant speed in glycerol, which has a viscosity of 1490 kg m^{-1} s^{-1}. The object has a mass of 0.00381 kg, has a radius of 0.00432 m, a mass of 0.00381 kg, and displaces a mass of fluid equal to 0.000337 kg. Find the speed of the object.

12. An object has a force on it given by $\mathbf{F} = (4.75\text{ N})\mathbf{i} + (7.00\text{ N})\mathbf{j} + (3.50\text{ N})\mathbf{k}$.

(a) Find the magnitude of the force.

(b) Find the projection of the force in the x-y plane. That is, find the vector in the x-y plane whose head is reached from the head of the force vector by moving in a direction perpendicular to the x-y plane.

13. An object of mass 12.000 kg is moving in the x direction. It has a gravitational force acting on it equal to $-mg\mathbf{k}$, where m is the mass of the object and g is the acceleration due to gravity, equal to 9.80 m s^{-1}. There is a frictional force equal to (0.240 N)$\mathbf{i}$. What is the magnitude and direction of the resultant force (the vector sum of the forces on the object)?

14. The potential energy of a magnetic dipole in a magnetic field is given by the scalar product

$$V = -\boldsymbol{\mu} \cdot \mathbf{B},$$

where $\mathbf{B}$ is the magnetic induction (magnetic field) and $\boldsymbol{\mu}$ is the magnetic dipole. Make a graph of $\frac{V}{|\boldsymbol{\mu}||\mathbf{B}|}$ as a function of the angle between $\boldsymbol{\mu}$ and $\mathbf{B}$ for values of the angle from 0° to 180°.

15. According to the Bohr theory of the hydrogen atom, the electron in the atom moves around the nucleus in one of various circular orbits with radius $r = a_0 n^2$, where a_0 is a distance equal to 5.29×10^{-11} m, called the Bohr radius, and n is a positive integer. The mass of the electron is 9.109×10^{-31} kg. According to the theory, the magnitude of the angular momentum, L, is equal to $nh/2\pi$, where h is Planck's constant, equal to 6.62608×10^{-34} J s. Find the speed of the electron for $n = 1$ and for $n = 2$.

Chapter 5

Problem Solving and the Solution of Algebraic Equations

Principal Facts and Ideas

- Solving an algebraic equation means finding the values of one or more variables such that the equation is satisfied.
- For a single independent variable, one equation is required to solve for a unique value of the variable.
- The solution or root to an algebraic equation is a value or a set of values of the independent variable such that substitution of such a value into the equation produces an numerically correct equation such as $0 = 0$.
- Polynomial equations through the fourth degree can be solved algebraically, but some equations of fifth and higher degree cannot be solved algebraically.
- One equation in two variables can be solved for one variable as a function of the other.
- To solve for two variables one must solve two equations simultaneously, but these equations must be independent and consistent.
- Linear homogeneous simultaneous equations have a nontrivial solution only when a certain dependence condition is met.

Objectives

After studying this chapter, you should be able to:

- solve any linear equation;
- solve a quadratic equation and determine which root is physically meaningful;
- obtain an accurate numerical approximation to the roots of one equation in one unknown, using graphical and numerical techniques;
- solve a set of two simultaneous linear equations.

5.1 ALGEBRAIC METHODS FOR SOLVING ONE EQUATION WITH ONE UNKNOWN

If you have one algebraic equation containing one variable, there will generally be a set of one or more constant values of that variable which make the equation valid. They are said to satisfy the equation, and the values in the set are called the *roots* or *solutions* of the equation.

5.1.1 Polynomial Equations

A *polynomial equation* is written in the form

$$f(x) = a_0 + a_1 x + a_2 x^2 + \cdots + a_n x^n = 0, \qquad (5.1)$$

where the as are constants. The integer n is called the *degree* of the equation. If $n = 1$, the equation is a *linear equation*. If $n = 2$, the equation is a *quadratic equation*. If $n = 3$, the equation is a *cubic equation*. If $n = 4$, it is a *quartic equation*, and so on. Generally, there are n roots to an nth-degree polynomial equation, but two or more of the roots can be equal to each other. For most equations arising from chemical problems, there will be only one root that is physically reasonable, and the others must be disregarded. For example, a concentration cannot be negative, and if a quadratic equation for a concentration produces a positive root and a negative root, the negative root must be disregarded. It is also possible for some of the roots to be imaginary or complex numbers. Complex roots cannot represent physically measurable quantities and must be disregarded if we are solving for a physically meaningful quantity.

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00005-7

Linear Equations

A linear equation is of the form

$$a_0 + a_1 x = 0. \tag{5.2}$$

This equation has a single root:

$$x = -\frac{a_0}{a_1}. \tag{5.3}$$

Quadratic Equations

A quadratic equation can be written in a standard form as

$$ax^2 + bx + c = 0. \tag{5.4}$$

A quadratic equation generally has two roots, which can be equal to each other. Some quadratic expressions can be factored, which means that the equation can be written

$$a(x - x_1)(x - x_2) = 0, \tag{5.5}$$

where x_1 and x_2 are the two roots of the equation. If a quadratic equation cannot easily be factored, you can apply the *quadratic formula*

$$\boxed{x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}}. \tag{5.6}$$

The quadratic formula delivers two roots, one when the positive sign in front of the square root is chosen and the other when the negative sign is chosen. There are three cases:

1. if the *discriminant* $b^2 - 4ac$ is positive, the roots will be real and unequal;
2. if the discriminant is equal to zero, the two roots will be real and equal to each other;
3. if the discriminant is negative, the roots will be complex and each root is the complex conjugate of the other root.

Exercise 5.1. Show by substitution that the quadratic formula provides the roots to a quadratic equation.

A common application of a quadratic equation in elementary chemistry is the calculation of the hydrogen-ion concentration in a solution of a weak acid. If activity coefficients are assumed to equal unity, the equilibrium expression in terms of *molar concentrations* is

$$K_a = \frac{([H^+]/c^\circ)([A^-]/c^\circ)}{[HA]/c^\circ}, \tag{5.7}$$

here $[H^+]$ represents the hydrogen-ion concentration expressed in mol l^{-1} (*molarity*), $[A^-]$ represents the acid-anion concentration, [HA] represents the concentration of the undissociated acid, the constant c° is defined to equal exactly 1 mol l^{-1}, and K_a represents the acid ionization constant. It is true that the hydrogen ions are nearly all attached to water molecules or water molecule dimers, and so on, so that we could write $[H_3O^+]$ instead of $[H^+]$, but this makes no difference in the calculation. The expression in terms of *molalities* (moles per kilogram of solvent) can also be used and has the same appearance.

Example 5.1. For acetic acid, $K_a = 1.754 \times 10^{-5}$ at 25 °C. Find $[H^+]$ if 0.1000 mol of acetic acid is dissolved in enough water to make 1.000 l of solution. We say that the *stoichiometric concentration* (the concentration that would occur if there were no ionization) is equal to 0.100 mol l^{-1}. Assume that activity coefficients are equal to unity.

If no other sources of hydrogen ions or acetate ions are present, $[H^+]/c^\circ = [A^-]/c^\circ$, which we denote by x,

$$K_a = \frac{x^2}{0.1000 - x}$$

or

$$x^2 + K_a x - 0.1000 K_a = 0.$$

From Eq. (5.6), our solution is

$$\begin{aligned} x &= \frac{-K_a \pm \sqrt{K_a^2 + 0.4000 K_a}}{2} \\ &= 1.316 \times 10^{-3} \text{ or } -1.333 \times 10^{-3}, \\ [H^+] &= [A^-] = 1.316 \times 10^{-3} \text{ mol } l^{-1}. \end{aligned}$$

We disregard the negative root because a concentration cannot be negative.

Exercise 5.2. For hydrocyanic acid (HCN), $K_a = 4.9 \times 10^{-10}$ at 25 °C. Find $[H^+]$ if 0.1000 mol of hydrocyanic acid is dissolved in enough water to make 1.000 l. Assume that activity coefficients are equal to unity and neglect hydrogen ions from water.

5.1.2 Approximate Solutions to Equations

Cubic and quartic polynomial equations can be solved algebraically, but it is probably best to apply approximation techniques rather than to attempt an algebraic solution.[1] Equations containing sines, cosines, logarithms, exponentials, and so on frequently must be solved by approximations. There are two approaches for obtaining an approximate solution to an equation. One approach is to approximate the equation by making simplifying assumptions, and the other is to seek a numerical approximation to the root.

[1] Older editions of *The Handbook of Chemistry and Physics* give methods for cubic equations. See, for example, the 33rd edition, pp. 272–273, Chem. Rubber Co., Cleveland, 1951–1952.

Approximation by Use of Simplifying Assumptions

As an example, let us consider an equation for the hydrogen-ion concentration in a solution of a weak acid in which the hydrogen ions from the ionization of water cannot be ignored. We must solve simultaneous equations for the ionization of the weak acid and ionization of water. If activity coefficients are assumed equal to unity, solution of the simultaneous equations gives the result:

$$K_a = \frac{x(x - K_w/x)}{c/c^\circ - x + K_w/x}, \tag{5.8}$$

where c is the stoichiometric concentration of the acid, where c° is defined to equal 1 mol l^{-1}, where K_w is the ionization constant of water, equal to 1.00×10^{-14} at 25 °C, and where $x = [H^+]/c^\circ$, and where we assume activity coefficients to equal unity. If we multiply this equation by x and collect the terms, we obtain the cubic equation

$$x^3 + K_a x^2 - \left(\frac{cK_a}{c^\circ} + K_w\right) x - K_a K_w = 0. \tag{5.9}$$

Exercise 5.3. Carry out the algebraic manipulations to obtain the cubic equation in Eq. (5.9).

Equation (5.9) can be solved numerically for any specific case.

Example 5.2. For acetic acid, $K_a = 1.754 \times 10^{-5}$ at 25 °C. Solve Eq. (5.9) numerically for acetic acid with a stoichiometric molarity of 1.000×10^{-5} mol l^{-1}.

By trial and error, we obtain $x = 0.711545 \times 10^{-5}$.

It is possible to simplify equations by making approximations.

Example 5.3. For the case of acetic acid with a stoichiometric concentration of 0.100 mol l^{-1}, convert Eq. (5.8) to a simpler approximate equation by discarding any negligible terms.

Equation (5.8) contains two terms in the numerator and three in the denominator. If one term in a polynomial is much smaller than the other terms, it might be possible to neglect this term. In the numerator, we know that in an acidic solution $x = [H^+]/c^\circ$ will lie somewhere between 0.1 and 10^{-7}, the value for pure water. In fact, we know from our approximate solution in the previous example that $[H^+]$ is near 10^{-3} mol l^{-1}. Since K_w equals 1.00×10^{-14}, the second term must be near 10^{-11} mol l^{-1}, which is smaller than the first term by a factor of 10^8. We therefore drop the term K_w/x. We also drop the same term in the denominator and obtain the equation

$$K_a = \frac{x^2}{(c/c^\circ) - x}, \tag{5.10}$$

which is the same as Eq. (5.7), with $[H^+] = [A^-] = x$.

It is possible in some cases to make a further approximation on Eq. (5.10). If only a small fraction of the weak acid ionizes, $[H^+]$ will be small compared with c, so that x can be neglected in the denominator. In the case of acetic acid and a gross acid concentration of 0.100 mol l^{-1}, $[H^+]$ is approximately equal to 10^{-3} mol l^{-1}, only about 1% as large as c. If we can tolerate an error of about 1%, we can neglect x compared with c/c°. We obtain

$$K_a = \frac{x^2}{c/c^\circ}, \tag{5.11}$$

which has the solution

$$x = \sqrt{(c/c^\circ)\, K_a}. \tag{5.12}$$

However, as c is made smaller, Eq. (5.11) quickly becomes a poor approximation, and for very small acid concentrations, Eq. (5.10) also becomes inaccurate. Table 5.1 shows the results from the three equations at different acid concentrations. Equation (5.10), the quadratic equation, remains fairly accurate down to $c = 10^{-5}$ mol l^{-1}, but Eq. (5.12) is wrong by about 7% at 10^{-3} mol l^{-1}, and much worse than that at lower concentrations.

Solution by Successive Approximations

In the case that approximations such as that of Eq. (5.12) are inaccurate, we can apply the method of *successive approximations*. In this method, one begins by solving an equation such as Eq. (5.12). The result of this approximation is used to approximate the term that was neglected in the first approximation, obtaining a second approximation. The result of this second approximation is used to replace the term that was originally neglected and a third approximation is obtained. This procedure is repeated (iterated) as many times as is necessary to obtain the desired accuracy.

Example 5.4. Solve the problem of Example 5.1 by successive approximation.

We write the equilibrium expression in the form

$$x^2 = K_a(0.1000 - x).$$

Since x is presumably much smaller than 0.1000 we neglect it compared with 0.1000. We obtain

$$x^2 \approx (1.754 \times 10^{-5})\,(0.1000) = (1.754 \times 10^{-6}),$$
$$x \approx 0.00132.$$

This is the result that would be obtained from Eq. (5.12). The next approximation is obtained by replacing the x in the right-hand side of the first equation by this value,

$$x^2 \approx (1.754 \times 10^{-5})(0.1000 - 0.00132)$$
$$= 1.731 \times 10^{-6},$$
$$x \approx \sqrt{1.731 \times 10^{-6}} = 0.001316 \approx 0.00132.$$

TABLE 5.1 Results for the Hydrogen-Ion Concentration in Acetic Acid Solutions from Different Equations at Different Concentrations

c (mol l^{-1})	Equation (5.9)	Equation (5.10)	Equation (5.12)
0.1000	1.31565×10^{-3}	1.31565×10^{-3}	1.324×10^{-3}
1.000×10^{-3}	1.23595×10^{-4}	1.23595×10^{-4}	1.324×10^{-4}
1.000×10^{-5}	0.71545×10^{-5}	0.71436×10^{-5}	1.324×10^{-5}
1.000×10^{-7}	0.161145×10^{-6}	0.099435×10^{-6}	1.324×10^{-6}

This result shows that the first approximation is acceptable. Further iterations would make even smaller changes, so we stop at this point.

Exercise 5.4. Solve for the hydrogen-ion concentration in solutions of acetic acid with stoichiometric molarities equal to 0.00100 mol l^{-1}. Use the method of successive approximations.

Approximation by Linearization

In the next example, we see another way in which an equation can be made into a tractable approximate equation, by linearizing a function. We illustrate this technique in the following example:

Example 5.5. The Dieterici equation of state is

$$Pe^{a/V_m RT}(V_m - b) = RT,$$

where P is the pressure, T is the temperature, V_m is the molar volume, and R is the ideal gas constant. For carbon dioxide, $a = 0.468$ Pa m^6 mol^{-2}, $b = 4.63 \times 10^{-5}$ m^3 mol^{-1}. Linearize the exponential and find the molar volume of carbon dioxide if $T = 298.15$ K and $P = 10.000$ atm $= 1.01325 \times 10^6$ Pa.

The exponential function can be represented by the power series

$$e^x = 1 + \frac{1}{1!}x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots,$$

where $n!$ stands for n factorial, defined as $n(n-1)$(n-2) $(n-3)\cdots(3)(2)(1)$ for $n \geq 1$ and $0! = 1$. We write

$$e^{a/V_m RT} = 1 + a/V_m RT + \frac{1}{2!}(a/V_m RT)^2 + \cdots.$$

Rough calculation shows that $a/V_m RT \approx 0.09$ so that $(a/V_m RT)^2 \approx 0.008$. We therefore discard all of the terms past the $a/V_m RT$ term and write to a fairly good approximation:

$$e^{a/V_m RT} \approx 1 + a/V_m RT.$$

We have linearized the exponential function. We substitute this approximation into the original equation of state, obtaining

$$P(1 + a/V_m RT)(V_m - b) = RT,$$

which can be written in the standard form for a quadratic equation:

$$PV_m^2 + \left(\frac{Pa}{RT} - Pb - RT\right)V_m - \frac{Pab}{RT} = 0.$$

We divide by P and substitute the numerical values. We temporarily let $x = V_m/(1\,\text{m}^3\ \text{mol}^{-1})$ and obtain after some manipulation

$$x^2 - (2.304 \times 10^{-3})x + 8.741 \times 10^{-9} = 0.$$

We apply the quadratic formula:

$$x = \frac{2.304 \times 10^{-3} \pm \sqrt{(0.002304)^2 - 4(8.741 \times 10^{-9})}}{2}$$
$$= \begin{cases} 2.30 \times 10^{-3}, \\ 4.000 \times 10^{-6}. \end{cases}$$

We disregard the second value as too small to correspond to the physical situation, and obtain

$$V_m = 2.30 \times 10^{-3}\ \text{m}^3\ \text{mol}^{-1}.$$

The ideal gas equation of state gives $V_m = 2.447 \times 10^{-3}$ m^3 mol^{-1}, for a difference of about 6%.

Exercise 5.5. Verify the prediction of the ideal gas equation of state given in the previous example.

Exercise 5.6. Substitute the value of the molar volume obtained in the previous example and the given temperature into the Dieterici equation of state to calculate the pressure. Compare the calculated pressure with 10.00 atm, to check the validity of the linearization approximation used in the example

5.2 NUMERICAL SOLUTION OF ALGEBRAIC EQUATIONS

Strictly speaking, one does not solve an equation numerically. One obtains an approximation to a root. However, with a computer or hand calculator, you can obtain enough significant digits for almost any purpose.

5.2.1 Graphical Solution of Algebraic Equations

We first discuss the *graphical method* to obtain a numerical approximation to the root or roots of an equation. This method is useful because you can see what you are doing and you can usually be sure that you do not obtain a different root than the one you want to find. The equation to be solved is written in the form

$$f(x) = 0. \tag{5.13}$$

If a graph of the function f is drawn, any real roots to the equation correspond to the places where the curve crosses the x axis.

Example 5.6. By constructing graphs, find the positive root of the cubic equation

$$x^3 - 0.6000x = 0.$$

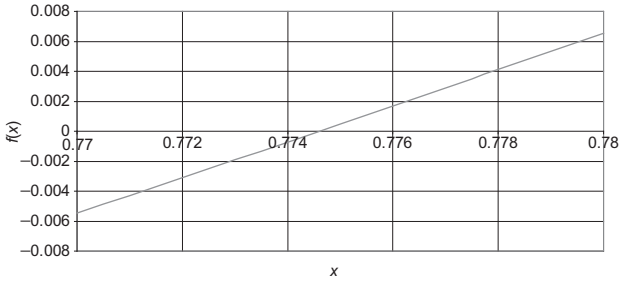
This cubic equation has three real roots, one of which is at $x = 0$.

We open a blank spreadsheet in Excel. We start by making a table of values of the function that is to vanish at the roots:

$$f(x) = x^3 - 0.6000x$$

in the range $-2 < x < 2$. We first type the value -2 in the cell A1. In cell A2 we type =A1 + 0.2 and press "Return." We then select an additional 20 cells in the first column by dragging the cursor over the cells while holding down the left mouse button, starting with the A2 cell and ending with the A21 cell. We press the "d" key while holding down the "Ctrl" key. This fills the first column with 21 values of x ranging from -2 to 2 in increments of 0.2. We then type the formula in cell B1 that will evaluate the polynomial, typing = A1^3–0.6* A1 and pressing the "enter" key. This inserts the formula into cell B1 and the places the value of the function (-6.8) in that cell. We then drag the cursor down the B column to B21, holding down the left mouse key, and then fill the cells with the formula by pressing the "d" key while holding down the "Ctrl" key. The values of the function appear in column B. Inspection of the values shows that the function changes sign three times in the interval, so all three of the roots lie in this region. We now construct a graph of the function. Inspection of the graph indicates that there are roots near $x = -0.77$, at $x = 0$, and near $x = 0.77$.

To locate the positive root more accurately, we construct a graph with a smaller range of x. We enter 0.77 in cell C1 and enter the formula = C1 + 0.0005 in cell C2. We then fill the formula down to cell C11. We then copy the formula in cell B1 and paste it into cell D1 and then fill the formula down to cell D21. We select columns C and D and make a second graph. This graph is shown below. The root appears to lie near $x = 0.7745$. To five significant digits, the correct value is $x = 0.77460$.



Exercise 5.7. Find approximately the smallest positive root of the equation

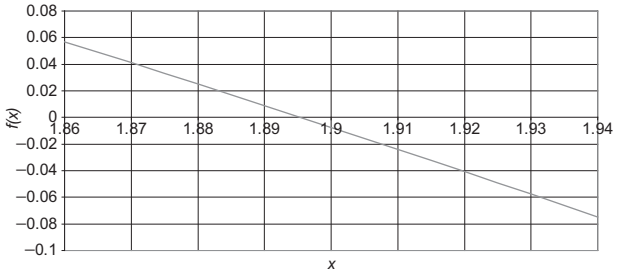
$$\tan(x) - x = 0.$$

Example 5.7. By graphing, find a root of the equation

$$2\sin(x) - x = 0.$$

in the interval $1.8 < x < 2.0$.

A graph of the function for the interval $1.86 < x < 1.94$ is shown below. From the graph, it appears that the root is near $x = 1.895$. To five significant digits, the correct value is $x = 1.8955$.



Exercise 5.8. Using a graphical procedure, find the most positive real root of the quartic equation:

$$x^4 - 4.500x^3 - 3.800x^2 - 17.100x + 20.000 = 0.$$

The curve representing this function crosses the x axis in only two places. This indicates that two of the four roots are complex numbers. Chemists are not usually interested in complex roots to equations.

5.2.2 Trial and Error

To apply this method, we typically write the equation in the form

$$f(x) = 0. \tag{5.14}$$

We repeatedly evaluate the function f, choosing different values of x, until f nearly vanishes. When using this method with a hand calculator or a spreadsheet, it is usually possible to adopt a strategy of finding two values of x such that f has different signs for the two values of x, and then to choose values of x within this interval until $f \approx 0$. If the equation has more than one root, you must make sure that you have found the applicable root.

Example 5.8. Use the method of trial and error to find the positive root of the equation

$$2\sin(x) - x = 0.$$

We let $f(x) = 2\sin(x) - x$, which vanishes at the root. We use the Excel spreadsheet to carry out the evaluation of the function $f(x)$. We put the formula in the B column, filling it down to enough rows for the number of times we think we will have to evaluate the function. We then put trial values into column A and inspect the value of the function in column B. We find quickly that $f(1) = 0.68294$, and that $f(2) = -0.1814$, so that there must be a root between $x = 1$ and $x = 2$. We find that $f(1.5) = 0.49499$, so the root lies between 1.5 and 2. We find that $f(1.75) = 0.21798$, so the root is larger than 1.75. However, $f(1.9) = -0.00740$, so the root is smaller than 1.9. We find that $f(1.89) = 0.00897$, so the root is between 1.89 and 1.90. We find that $f(1.895) = 0.000809$ and that $f(1.896) = -0.000829$. To five significant digits, the root is $x = 1.8955$.

Exercise 5.9. Use the method of trial and error to find the two positive roots of the equation

$$e^x - 3.000x = 0$$

to five significant digits. Begin by making a graph of the function to find the approximate locations of the roots.

5.2.3 The Method of Bisection

This is a systematic version of the trial and error method. You start with two values of x for which the function $f(x)$ has opposite signs, and then evaluate the function for the midpoint of the interval and determine which half of the interval contains the root. The midpoint of the half of the original interval containing the root is taken, and it is determined which half of this new interval contains the root. The method is continued, repeating the process until the interval known to contain the root is as small as twice the error you are willing to tolerate. The middle of the last interval is then taken as the approximation to the root.

5.2.4 Solving Equations Numerically with Excel

Excel is a large and versatile program, and we do not have the space to discuss all of its capabilities. It has the capability to solve equations numerically, using a command called *Goal Seek*. This command causes the software to change a variable until a defined function of that variable attains a specified value. It uses a method called the Newton-Raphson method, which we will discuss in a later chapter. This method begins with a trial value of the independent variable and varies it to find the root. If there is more than one root, you must select a trial value not too far from the desired root. To use this function, you open Excel, select a cell, and enter a trial value of the independent variable. Select another cell and enter a formula giving the function that you want to equal zero (or whatever value you need). Use the address of the trial value in this formula. Now click on the tab labeled "Data" in the ribbon at the top of the window. Click on the icon labeled "What-If Analysis," which gives you three options. Click on "Goal Seek." A window opens up with three boxes. In the top box you specify the address of the cell in which your formula is entered. In the second box, you enter the value you want the function to attain, and in the third box you enter address of the cell where you entered the trial value of the root. Click on OK and the computer does the analysis and places the root in the cell in which you put the trial value. We illustrate the process in the following example.

Example 5.9. Using Excel, find the real roots of the equation

$$x^4 - 5x^3 + 4x^2 - 3x + 2 = 0.$$

We determine by graphing that there is a real root near $x = 1$ and a real root near $x = 4$. To find the first root, we enter the trial value 1 in cell A1 and type the following formula in cell B1: =A1 ^4–5*A1^3 + 4*A1^2–3*A1 + 2 and press the "Return" key. We click on the "Data" tab and then click on the "What-If Analysis" icon. A window appears, and we select "Goal Seek" in that window. A window appears with three blanks. The first says "Set cell:" and we enter the address B1 in the blank. The second blank says "To value:" and we type in a zero, since we want the function to attain the value zero. The third blank says "By changing cell:" We type in A1, since that is the cell containing our trial root. We click on "OK" and the software quickly finds the root and places the value of the root, 0.802 309, in cell A1. We then repeat the process with a trial value of 4 in cell A1. The software quickly places the value of root, 4. 188 847 in cell A1.

Exercise 5.10. Use Excel to find the real root of the equation

$$x^3 + 5.000x - 42.00 = 0.$$

5.3 A BRIEF INTRODUCTION TO MATHEMATICA

Mathematica is a complete mathematics package that can carry out both numerical and symbolic mathematics. When you open Mathematica, a blank "untitled" window appears on the video screen. This window is called a *notebook*. Mathematica is now ready to accept instructions.

5.3.1 Numerical Calculations with Mathematica

You can use Mathematica to make numerical calculations much as you would use a calculator. In an open notebook, you can type in numbers and symbols for arithmetic operations:

addition: +
subtraction: −
negation: −
division: /
multiplication: blank space or asterisk (∗)
exponentiation: ^
factorial: !
Parentheses are used in the same way as in writing ordinary formulas.

Numbers in scientific notation are entered in a fairly obvious way. To enter 1.234×10^4, you would type 1.234 10^4 with the space standing for multiplication, or 1.234 ∗ 10^4. In the output lines, Mathematica always uses the space for multiplication.

Most of the Mathematica symbols are the same as those used in Excel or various computer programming languages such as BASIC except for the use of a blank space for multiplication. Excel and BASIC use only the asterisk for multiplication. In Mathematica, if you write *xy*, the software will think you mean a variable called *xy*, not the product of *x* and *y*. However, you can write either 2*x* or 2 *x* for 2 times *x*, but not *x*2. It is probably best to use the asterisk (∗) for multiplication rather than a space in input statements. Watch for the use of the blank space in output statements. Complex arithmetic is done automatically, using the capital letter I for $\sqrt{-1}$. Several constants are available by using symbols: Pi, E, I, Infinity, and Degree stand for π, e, $i = \sqrt{-1}$, ∞, and $\pi/180$ (conversion from degrees to radians). The first letter of each symbol must be capitalized.

For example, to obtain $(4.67841 + 3.58731)^{56.3}$, you type in an open notebook the following expression:

```
(4.67841 + 3.58731)^56.3
```

using the caret (^) to stand for exponentiation. Parentheses are used to determine the sequence of operations. The rule is that all operations inside a pair of parentheses will be carried out before the result is combined with anything else. After you type an input statement, you then press the "Enter" key (the "Enter" key at the far right of the keyboard in the number keypad, not the "Return" key in the main part of the keyboard, which is also labeled "Enter" on some keyboards). Instead of pressing the "Enter" key, you can press the "Return" key in the main part of the keyboard while holding down the "Shift" key (a "Shift-Return"). If you press the "Return" key without the "Shift" key, you are signaling Mathematica that you are continuing one statement onto a second line. When you press the "Enter" key, you are ending a unit called a "cell."

Mathematica labels each input cell by a number. If you are at the beginning of a notebook, after you press the "Enter" key you will see

```
In[1]: =(4.67841 + 3.58731)^56.3
```

Mathematica prints input in bold-face type. When you press the "Enter" key, it will immediately print out the result, labeling it as output number 1:

```
Out[1]=4.39443 10^51
```

In this expression, the space before the 10 stands for multiplication.

On the screen there is now a square bracket at the right of your input and another at the right of the output, as well as a larger square bracket to the right of both of these brackets and encompassing them. The smaller brackets identify the cells. Mathematica assumes that any new cell is an input cell. When you press the "Enter" key, you notify Mathematica that you are ending the input cell, and that you want any expression in the input cell to be evaluated. When Mathematica prints your output, it creates an output cell for the output, and prints a larger bracket linking the input cell with its output cell. Any Mathematica notebook consists of a sequence of cells, which are numbered sequentially.

Pressing the "Return" key in the main part of a keyboard does not end a cell. If a piece of input requires more than one line, you can press the "Return" key at the end of each line, and then press the "Enter" key or the "Shift-Enter" at the end of the cell. You can put several executable statements in the same cell. It is best to separate them by pressing the "Return" key after each statement.

Many functions are available in Mathematica. The names of the functions must be entered with the first letter capitalized and sometimes a letter in the middle capitalized. The other letters must be in lower case and the argument of the function must be enclosed in square brackets, not parentheses. You will have to get used to this. No deviation from the capitalization rule is allowed, and Mathematica will not recognize parentheses instead of brackets. Some common functions are given in Table 5.2. Other functions

TABLE 5.2 Mathematical Functions in Mathematica

Symbol	Function	Result
Abs[x]	absolute value (magnitude) of x	nonzero constant
Arg[z]	argument ϕ of complex expression $\lvert z\rvert e^{i\phi}$	nonzero constant
ArcCos[x]	inverse cosine in radians	constant, $0 < c < \pi$
ArcSin[x]	inverse sine in radians	constant, $-\frac{\pi}{2} < c < \frac{\pi}{2}$
ArcTan[x]	inverse tangent in radians	constant, $-\frac{\pi}{2} < c < \frac{\pi}{2}$
Conjugate[z]	complex conjugate of $z = x + iy$	$x - iy$
Cos[x]	cosine of an angle in radians	constant, $-1 < c < 1$
Exp[x]	exponential function, e^x	positive constant
Im[z]	imaginary part of complex expression z	constant
Log[x]	natural logarithm (base e)	constant
Log[b,x]	logarithm to the base b	constant
n!	n factorial	constant
Random[ ]	random number generator	constant, $0 < c < 1$
Re[z]	real part of complex expression z	constant
Round[x]	closest integer to x	constant
Sin[x]	sine of an angle in radians	constant, $-1 < c < 1$
Sqrt[x]	square root of x	constant
Tan[x]	tangent of an angle in radians	constant

are described in the book by Wolfram listed at the end of the chapter.

Exercise 5.11. Write Mathematica expressions for the following:

(a) The complex conjugate of $(10)e^{2.657i}$.
(b) $\ln(100!) - (100\ln(100) - 100)$.
(c) The complex conjugate of $(1 + 2i)^{2.5}$.

Mathematica will print out numerical values with any specified number of digits. You enter the letter N followed by the expression, then a comma, and then the number of digits desired. For example, if you want to have the value of $(3.58731)^{56.3}$ to 15 digits, you use the input statement.

```
N[3.58731^56.3,15]
```

and press the "Enter" key. Mathematica will print

```
In[1]:=N[3.58731^56.3,15]
Out[1]=1.71194390461979 10^31
```

The entire expression and the number of digits are enclosed in the square brackets following the N. If you do not specify the number of digits, Mathematica will give you a standard number of digits (usually six) for an expression that contains a decimal point. It will give all of the digits if possible for an expression that does not contain a decimal point. If you enter 30!, it will give you the entire value, with 33 digits. If you enter 30.! it will give you a value with six digits. However, if you enter Sqrt[3], it will not give you a value, since an exact value of 3 cannot be written with a finite number of digits. It will print Sqrt[3] as output. If you enter Sqrt[3.], it will give you a value with six digits, and you can also get a six-digit answer by entering N[Sqrt[3]] or Sqrt[3]//N. If you want 20 digits, you can enter N[Sqrt[3],20].

You can refer to the last output cell with a percent sign (%) or to any other output cell by its number following a percent sign. If you want to refer to output cell number 3, you would type %3. If you had entered Sqrt[3] and had obtained Sqrt[3] as your output, you could type N[%] and press the enter key to obtain a numerical value with six digits, or could type N[%,15] to obtain a numerical value with 15 digits.

Mathematica statements can contain symbols for stored *variables* as well as constants. A variable stands for a location in the computer memory in which a numerical value can be stored. Variable names can contain any number of letters and/or digits. However, they cannot begin with a

digit. Begin your variable names with a lower-case letter to avoid confusion with Mathematica functions and other Mathematica objects, which always begin with a capital letter. Also remember that xy would represent a variable called xy while x y (with a space between the letters) stands for the product of the two variables x and y.

Values are assigned to variables by using an ordinary equal sign, which stands for an *assignment operator*. For example, a value of 75.68 would be assigned to the variable x by entering the statement:

```
x = 75.68
```

and pressing the "Enter" key. The variable x will be replaced by the value 75.68 whenever it occurs in a Mathematica expression until a new value is assigned. To remove a value from the variable x, type the statement

```
Clear[x].
```

If you are not sure whether a given variable already has a value, use the *Clear statement* before using the variable.

You can also define one variable in terms of other variables. Assuming that x already has a value, the statement.

```
y = x^3
```

will assign the cube of the value of x to the variable y. The variable y will keep that numerical value until it is explicitly assigned a new value, even if the value of x is changed. You can also define y as a function of x such that the value of y will change if a new value of x is assigned. To do this, you use the second type of equal sign that is used in Mathematica, denoted by the symbol := (a colon followed by an equal sign). The statement

```
y:=x^3
```

will cause y to be evaluated as the cube of whatever value x has at the time of execution. You can see what the value of any variable is at the moment by typing the name of the variable and pressing the enter key. If you type a question mark followed by the name of the variable and press the enter key, you can see whether it is defined as a function of other variables.

You can also define a function. For example, say that you want to define the function

$$f = abce^{-x/y},$$

where a, b, and c are constants and x and y are variables. You can type

```
Clear[a,b,c,f,x,y]
f[x_]:=a b c Exp[-x/y]
```

where we have used the space to stand for multiplication. You can also type

```
Clear[a,b,c,f,x,y]
f[x_]:=a*b*c*Exp[-x/y]
```

The underscore following the symbol for the independent variable in the function expression on the left-hand side of the statement is part of the function definition and must be typed in. Mathematica's second type of equal sign, :=, (a colon followed by an equal sign), must be used. After defining a function, you can use it in a Mathematica expression, as in the statement.

```
g = x*f[x]*Cos[x/y]
```

The underline is used only in the definition of the function. It is not used after the symbol for the function's argument in an expression. Note that Mathematica uses square brackets for the argument of a function, not parentheses. The rules of Mathematica must be followed exactly. There is no provision for alternative symbols.

A cell can also be designated as a text cell, allowing Mathematica to be used like a word processor. You can convert any cell to a text cell as follows: first "select" the cell by placing the mouse cursor on the bracket to the right of the cell and pressing on the mouse button (clicking on the bracket). Then type the numeral 7 while depressing the "Alt" key. Mathematica will store text in a text cell, but will not perform any mathematical operations on anything in a text cell. You can delete the contents of any cell by selecting the cell and then choosing "Clear" from the "Edit" menu or typing the letter x while depressing the "Ctrl" key.

5.3.2 Symbolic Algebra with Mathematica

Mathematica has a powerful capability to carry out symbolic mathematics on algebraic expressions and can solve equations symbolically. In addition to the arithmetic operations, the principal Mathematica statements for manipulating algebraic expressions are Expand[ ], Factor[ ], Simplify[ ], Together[ ], and Apart[ ]. The *Expand* statement multiplies factors and powers out to give an expanded form of the expression. The following input and output illustrate this action:

```
In[1]:=Clear[a,x]
  Expand[(a + x) ^3]
Out[1] = a^3 + 3 a^2 x + 3 a x^2 + x^3
```

The *Clear* statement is included in case a and x had been previously defined as variables with specific values, which would cause Mathematica to return a numerical result instead of a symbolic result.

The *Factor* statement manipulates the expression into a product of factors. The following input and output illustrate this action:

```
In[2]:=Clear[y]
  Factor[1 + 5 y + 6 y^2]
Out[2] = (1 + 2 y) (1 + 3 y)
```

Note the use of the blank space for multiplication. Note also that the *Factor* statement does not have its own input line number, because the "Return" key was pressed after the *Clear* statement, not the "Enter" key. The *Simplify* statement manipulates an expression into the form that is considered by the rules built into Mathematica to be the simplest form (with the fewest parts). This form might be the factored form or the expanded form, depending on the expression.

The *Together* statement collects all terms of an expression together over a common denominator, while the *Apart* statement breaks the expression apart into terms with simple denominators, as in the method of *partial fractions*. The theorem of partial fractions states that if $Q(x)$ can be factored in the form

$$Q(x) = (a_1x + b_1)(a_2x + b_2)(a_3x + b_3)\cdots(a_nx + b_n), \tag{5.15}$$

where all the *a*s and *b*s are constants and if *P(x)* is of lower degree than *Q(x)*, then

$$\boxed{\frac{P(x)}{Q(x)} = \frac{A_1}{a_1x + b_1} + \frac{A_2}{a_2x + b_2} + \cdots + \frac{A_n}{a_nx + b_n}}, \tag{5.16}$$

where $A_1, A_2, \ldots, A_n$ are all constants.

Example 5.10. Write a Mathematica entry that will carry out the decomposition into partial fractions of the expression

$$\frac{6x - 30}{x^2 + 3x + 2}.$$

The input and output lines are:

```
In[1]: = Clear[x]
  Apart[(6 x − 30)/(x^2 + 3 x + 2)]
Out[1] =−36/(1 + x) + 42/(2 + x)
```

Exercise 5.12. In the study of the rate of the chemical reaction of substances A and B:

$$a\mathrm{A} + b\mathrm{B} \rightarrow \text{products},$$

the quotient occurs.

$$\frac{1}{([\mathrm{A}]_0 - ax)([\mathrm{B}]_0 - bx)},$$

where $[\mathrm{A}]_0$ and $[\mathrm{B}]_0$ are the initial concentrations of A and B, a and b are the stoichiometric coefficients of these reactants, and x is a variable specifying the extent to which the reaction has occurred. Write a Mathematica statement to decompose the denominator into partial fractions.

5.3.3 Solving Equations with Mathematica

Mathematica can carry out both symbolic and numerical solutions of equations, including single algebraic equations, simultaneous algebraic equations, and differential equations, which we discuss later. Mathematica contains the rules needed for the symbolic solution of polynomial equations up to the fourth degree, and can solve some fifth-degree equations. The principal statements used to solve equations are Solve, FindRoot, Eliminate, and Reduce.

The *Solve* statement returns symbolic formulas for solutions, if they exist. For example, the input line to solve the equation $ax^2 + bx + c = 0$ is

```
In[1]: =Solve[a*x^2 + b*x + c= =0,x]
```

The name of the variable to be solved for must be included at the end of the equation and separated from it by a comma. Mathematica's third kind of equal sign, a double equal sign, must be used in equations to be solved. Another use of this equal sign is in asking Mathematica to test whether an equality is true or false.

The resulting output is the standard quadratic formula:

$$\text{Out[1]} = \left\{\left\{\mathrm{x}\rightarrow \frac{-b - \mathrm{Sqrt}\left[b^2 - 4ac\right]}{2a}\right\}, \left\{\mathrm{x} \rightarrow \frac{-b + \mathrm{Sqrt}\left[b^2 - 4ac\right]}{2a}\right\}\right\}.$$

Note the use of the arrow symbol ($\rightarrow$).

If no formula can be found for a solution, you can use the *FindRoot* statement to obtain a numerical value for the root. You must provide a first estimate of the root (a). For example, to find a root for the equation

$$e^{-x} - 0.5x = 0$$

with a trial root of $x = 1$, you type the input statement:

```
In[1]:=FindRoot[Exp[−x] − 0.5∗ x == 0,{x,1}]
```

and get the output

```
Out[1] = {x → 0.852606}
```

The trial value of the root is here represented by the 1 following the x in braces (curly parentheses, $\{\cdots\}$). If your equation is a polynomial equation, the *NSolve* statement can be used instead of FindRoot. The *NSolve* statement does not require a trial root, and will find all roots, while the *FindRoot* statement will generally cause Mathematica to converge to one root and then stop. If your equation has more than one root, you need to determine whether you have found the desired root and not one of the others.

Example 5.11. Using the *NSolve* statement find the roots of the equation

$$x^4 - 5.00x^3 + 4.00x^2 - 3.00x + 2.00 = 0.$$

We enter the input statement.

```
NSolve[x ^4 − 5 x^3 + 4 x^2 − 3 x + 2==0,x]
```

We press the "Enter" key and receive the output.

```
Out[1] = {{x -> 0.00442308–0.771419ii,
          {x -> 0.00442308  + 0.771419ii,
         {x -> 0.802307}, {x -> 4.18885}}
```

where Mathematica uses the a symbol that looks like double i (ii with a single dot) to represent the imaginary unit in its output statement. Use a capital I in an input statement to stand for the square root of -1.

Exercise 5.13. Verify the real solutions in the preceding example by substituting them into the equation.

Exercise 5.14. Use the NSolve statement in Mathematica to find the numerical values of the roots of the equation

$$x^3 + 5.000x - 42.00 = 0.$$

Use the FindRoot statement to find the real root of the same equation.

5.3.4 Graphing with Mathematica

Mathematica can produce sophisticated graphs, including two-dimensional graphs and perspective views of three-dimensional graphs. Graphing a function is easier than with Excel, since you do not have to fill columns with values of the variable.

Example 5.12. Make a graph of $\sin(x)$ from $x = 0$ to $x = 2\pi$,

We enter the input.

```
Plot[Sin[x],{x,0,2Pi}]
```

and press the "Enter" key. The graph appears on the computer screen in an output statement.

The graphic capabilities of Mathematica are very extensive. For example, it makes perspective views of three-dimensional graphs. You can read more about this in the book by Wolfram and in the manual that is supplied with Mathematica.

5.4 SIMULTANEOUS EQUATIONS: TWO EQUATIONS WITH TWO UNKNOWNS

The simplest type of simultaneous equations is the set of two equations:

$$a_{11}x + a_{12}y = c_1, \tag{5.17a}$$
$$a_{21}x + a_{22}y = c_2, \tag{5.17b}$$

where the as and the cs are constants. This set of equations is called *linear* because the unknowns x and y enter only to the first power, and is called *inhomogeneous*, because there are terms that do not contain x or y. If certain conditions are met, such a set of equations can be solved for a solution set consisting of a single value of x and a single value of y.

5.4.1 The Method of Substitution

The first step of this method is to solve one equation to give one variable as a function of the other. You can then substitute this function into the other equation to give an equation in one unknown. You can substitute the solution of this equation into either of the original equations and solve for the second variable.

Example 5.13. Use the method of substitution on the simultaneous equations in Eqs. (5.17a) and (5.17b)

We solve the first equation for y in terms of x:

$$y = \frac{c_1}{a_{12}} - \frac{a_{11}x}{a_{12}}.$$

We substitute this into the second equation to obtain the linear equation in x:

$$a_{21}x + a_{22}\left(\frac{c_1}{a_{12}} - \frac{a_{11}x}{a_{12}}\right) = c_2,$$
$$a_{21}x - a_{22}\frac{a_{11}x}{a_{12}} = c_2 - a_{22}\frac{c_1}{a_{12}}.$$

This contains only x and not y, so it can be solved for x to give the root

$$x = \frac{c_1a_{22} - c_2a_{12}}{a_{11}a_{22} - a_{12}a_{21}}.$$

This expression can be substituted into one of our original equations and solved for y to yield

$$y = \frac{c_2a_{11} - c_1a_{21}}{a_{11}a_{22} - a_{12}a_{21}}.$$

If the denominator of this fraction vanishes, this solution is not valid.

The method of substitution is not limited to two equations and is not limited to linear equations.

Example 5.14. Solve the following equations:

$$x^2 - 2xy - x = 0,$$
$$x + y = 2.$$

We solve the second equation for y in terms of x to obtain

$$y = 2 - x.$$

We substitute this into the first equation to obtain an equation in one unknown

$$x^2 - 4x + 2x^2 - x = 0,$$
$$3x^2 - 5x = 0.$$

Since we can factor x out of this equation, we have two solutions:

$$x = 0$$

and

$$x = \frac{5}{3}.$$

We substitute each of these into the first equation. The first solution set is

$$x = 0, \quad y = 2.$$

The second solution set is

$$x = \frac{5}{3}, \quad y = \frac{1}{3}.$$

In this example there are two solution sets, since the first equation is quadratic in x.

Exercise 5.15. Solve the simultaneous equations by the method of substitution:

$$x^2 - 2xy - x = 0,$$
$$x + y = 0.$$

5.4.2 The Method of Elimination

This method consists of the process of subtracting one equation from another to obtain a simpler equation. If necessary, we can multiply each equation by a constant before subtracting.

Example 5.15. Solve the following pair of equations:

$$x + y = 3,$$
$$2x + y = 0.$$

We subtract the first equation from the second to obtain

$$x = -3.$$

This is substituted into either of the original equations to obtain

$$y = 6.$$

Exercise 5.16. Solve the set of equations

$$3x + 2y = 40,$$
$$2x - y = 10.$$

5.4.3 Consistency and Independence in Simultaneous Equations

There are two common difficulties that can arise with pairs of simultaneous inhomogeneous equations: these are (1) that the equations might be inconsistent and (2) that the equations might not be independent. If two equations are *inconsistent*, there is no solution that can satisfy both of them. If the equations are not independent, they express the same information, so that there is really only one equation, which can be solved for one variable in terms of the other but cannot be solved to give numerical values for both variables.

Example 5.16. Show that the pair of equations is inconsistent:

$$2x + 3y = 15,$$
$$4x + 6y = 45.$$

We attempt a solution by elimination. We multiply the first equation by 2 and subtract the second from the first, obtaining

$$0 = -15,$$

which is obviously not correct. The equations are inconsistent.

Example 5.17. Show that the equations are not independent:

$$3x + 4y = 7,$$
$$6x + 8y = 14.$$

We attempt a solution by elimination, multiplying the first equation by 2. We have just one independent equation instead of two, so that we could solve for x in terms of y or for y in terms of x, but not for numerical values of either x or y.

We can understand consistency and independence in simultaneous equations by looking at the graphs of the equations. Each of the graphs represents y as a linear function of x.

Figure 5.1 shows the lines representing two consistent and independent equations. The lines cross at the point whose coordinates represent the solution, consisting of a value of x and a value of y that satisfy the equations.

Figure 5.2 shows the lines representing two inconsistent equations. Since the lines do not cross, there is no solution to this pair of inconsistent equations. A single line represents two equations that are not independent. Any point on the line satisfies both equations. The line represent y as a function of x.

5.4.4 Homogeneous Linear Equations

A pair of *homogeneous linear equations* can be written in the form:

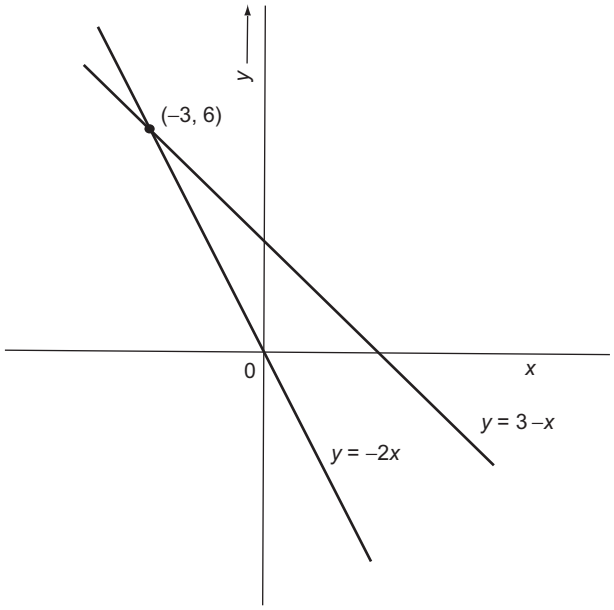


FIGURE 5.1 Graphical representation of the two consistent and linearly independent equations of Example 5.15.

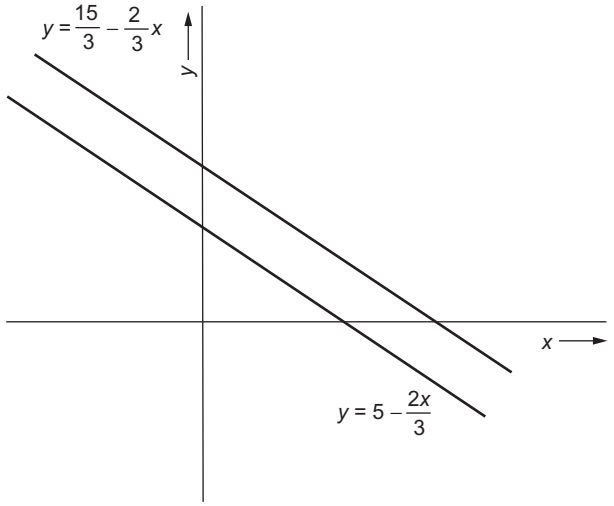


FIGURE 5.2 Graphical representation of the two inconsistent equations of Example 5.16.

$$a_{11}x + a_{12}y = 0, \tag{5.18a}$$
$$a_{21}x + a_{22}y = 0. \tag{5.18b}$$

We solve both of these equations for y in terms of x:

$$y = \frac{-a_{11}x}{a_{12}}, \tag{5.19}$$
$$y = \frac{-a_{21}x}{a_{22}}. \tag{5.20}$$

Both of these functions are represented by straight lines with zero intercept. There are two possibilities: Either the lines cross at the origin or they coincide everywhere. In other words, either $x = 0$, $y = 0$ is the solution, or else the equations are linearly dependent (are the same equation). The solution $x = 0$, $y = 0$ is called a *trivial solution*. The two equations must be linearly dependent in order for a nontrivial solution to exist, so that there is really only one equation. A nontrivial solution consists of specifying y as a function of x, not in finding constant values for both x and y.

Example 5.18. Determine whether the set of equations has a nontrivial solution, and find the solution if it exists:

$$7x + 15y = 0,$$
$$101x + 195y = 0.$$

From the first equation

$$y = -\frac{7x}{15} = -0.46667x.$$

From the second equation

$$y = -\frac{101x}{195} = -0.51785x.$$

These two equations are represented by lines that cross at the origin, so there is no nontrivial solution.

Exercise 5.17. Determine whether the set of equations has a nontrivial solution, and find the solution if it exists

$$5x + 12y = 0,$$
$$15x + 36y = 0.$$

5.4.5 Using Mathematica to Solve Simultaneous Equations

The *Solve* statement can also be used to solve simultaneous equations as well as single equations. The equations are typed inside curly brackets with commas between them, and the variables are listed inside curly brackets.

Example 5.19. Solve the equations

$$ax + by = c,$$
$$gx + hy = k.$$

We type the input entry

```
In[1]:=Solve[{a*x + b*y == c,g*x + h*y == k},{x,y}]
```

The output is

$$\text{Out[1]} = \left\{\left\{x \to -\frac{-ch + bk}{-bg + ah}, y \to -\frac{-cg + ak}{bg - ah}\right\}\right\}$$

Blank spaces could be used instead of the asterisks to denote multiplication. Braces (curly brackets) are used to notify Mathematica that we have a list of two equations to be solved. The two variables to be solved for must be included inside braces. If numerical values for the coefficients are specified, Mathematica will give the numerical solution set.

Exercise 5.18. Use Mathematica to solve the simultaneous equations

$$\begin{aligned} 2x + 3y &= 13, \\ x - 4y &= -10. \end{aligned}$$

The *Eliminate* statement is used to eliminate one or more of the variables in a set of simultaneous equations. For example, to obtain a single equation in x from the set of equations above, you would type the input entry (note the double equal signs):

```
Eliminate[{a x  + b y == c, g x  + h y == k},y]
```

and would receive the output:

```
Out[1] = b k  −  b g x  + a h x == c h
```

we solve this equation for x by typing

```
Solve[%,x]
```

and receive the output

$$\text{Out[2]=}\left\{\left\{x \to \frac{-ch + bk}{bg - ah}\right\}\right\}$$

PROBLEMS

1. Solve the quadratic equations:

(a) $x^2 - 3x + 2 = 0$.
(b) $x^2 - 1 = 0$.
(c) $x^2 + 2x + 2 = 0$.

2. Solve the following equations by factoring:

(a) $x^3 + x^2 - x - 1 = 0$.
(b) $x^4 - 1 = 0$.

3. Rewrite the factored quadratic equation $(x - x_1)(x - x_2) = 0$ in the form $x^2 - (x_1 + x_2)x + x_{12}x = 0$. Apply the quadratic formula to this version and show that the roots are $x = x_1$ and $x = x_2$.

4. The pH is defined for our present purposes as

$$\text{pH} = -\log_{10}([\text{H}^+]/\text{c}^\circ).$$

Find the pH of a solution formed from 0.075 mol of NH_3 and enough water to make 1.00 l of solution. The ionization that occurs is

$$\text{NH}_3 + \text{H}_2\text{O} \leftrightarrows \text{NH}_4^+ + \text{OH}^-.$$

The equilibrium expression in terms of molar concentrations is

$$\begin{aligned} K_\text{b} &= \frac{([\text{NH}_4^+]/\text{c}^\circ)([\text{OH}^-]/\text{c}^\circ)}{x(\text{H}_2\text{O})([\text{NH}_3]/\text{c}^\circ)} \\ &\approx \frac{([\text{NH}_4^+]/\text{c}^\circ)([\text{OH}^-]/\text{c}^\circ)}{([\text{NH}_3]/\text{c}^\circ)}, \end{aligned}$$

where $x(\text{H}_2\text{O})$ represents the mole fraction of water, which is customarily used instead of its molar concentration. Since the mole fraction of the solvent in a dilute solution is nearly equal to unity, we can use the approximate version of the equation. The base ionization constant of NH_3, denoted by K_b, equals 1.80×10^{-5}at at 25 °C.

5. The acid ionization constant of chloroacetic acid is equal to 1.40×10^{-3} at 25 °C. Assume that activity coefficients are equal to unity and find the hydrogen-ion concentration at the following stoichiometric molarities:

(a) 0.100 mol l^{-1}.
(b) 0.0100 mol l^{-1}.

6. Find the real roots of the following equations by graphing:

(a) $x^3 - x^2 + x - 1 = 0$.
(b) $e^{-x} - 0.5x = 0$.
(c) $\sin(x)/x - 0.75 = 0$.

7. Make a properly labeled graph of the function $y(x) = \ln(x) + \cos(x)$ for values of x from 0 to 2.

(a) Use Excel.
(b) Use Mathematica.

8. When expressed in terms of "reduced variables," the van der Waals equation of state is

$$\left(P_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \frac{8T_r}{3}.$$

(a) Using Excel, construct a graph containing three curves of P_r as a function of V_r: for the range $0.4 < V_r < 2$:one for $T_r = 0.6$, one for $T_r = 1$, and one for $T_r = 1.4$.
(b) Repeat part a using Mathematica.

9. Using a graphical method, find the two positive roots of the following equation.

$$e^x - 3.000x = 0.$$

10. The following data were taken for the thermal decomposition of N_2O_3 at a constant temperature:

t/s	0	184	426	867	1877
$[N_2O_3]$/mol l^{-1}	2.33	2.08	1.67	1.36	0.72

Using Excel, make three graphs: one with $\ln([N_2O_3])$ as a function of t, one with $1/[N_2O_3]$ as a function of t, and one with $1/[N_2O_3]^2$ as a function of t. Determine which graph is most nearly linear. If the first graph is most nearly linear, the reaction is first order; if the second graph is most nearly linear, the reaction is second order, and if the third graph is most nearly linear, the reaction is third order.

11. Write an Excel worksheet that will convert a list of distance measurements in meters to miles, feet, and inches. If the length in meters is typed into a cell in column A, let the corresponding length in miles appear on the same line in column B, the length in feet in column C, and the length in inches in column C.

12. The van der Waals equation of state is

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT,$$

where a and b are temperature-independent parameters that have different values for each gas. For carbon dioxide, $a = 0.3640$ Pa m^6 mol^{-2} and $b = 4.267 \times 10^{-5}$ m^3 mol^{-1}.

(a) Write this equation as a cubic equation in V.
(b) Use the *NSolve* statement in Mathematica to find the volume of 1.000 mol of carbon dioxide at $P = 1.000$ bar (100000 Pa) and $T = 298.15$ K. Notice that two of the three roots are complex and must be ignored. Compare your result with the prediction of the ideal gas equation of state.
(c) Use the *FindRoot* statement in Mathematica to find the real root in part b.
(d) Repeat part b for $P = 10.000$ bar (1.0000×10^6 Pa) and T = 298.15 K. Compare your result with the prediction of the ideal gas equation of state.

13. An approximate equation for the ionization of a weak acid, including consideration of the hydrogen ions from water is[2]

$$[H^+]/c^\circ = \sqrt{K_a c/c^\circ + K_w},$$

where c is the gross acid concentration. This equation is based on the assumption that the concentration of unionized acid is approximately equal to the gross acid concentration. Consider a solution of HCN (hydrocyanic acid) with stoichiometric acid concentration equal to 1.00×10^{-5} mol l^{-1}. $K_a = 4 \times 10^{-10}$ for HCN. At this temperature, $K_w = 1.00 \times 10^{-14}$.

(a) Calculate $[H^+]/c^\circ$ using this equation.
(b) Calculate $[H^+]/c^\circ$ using Eq. (5.9).

14. Find the smallest positive root of the equation.

$$\sinh(x) - x^2 - x = 0.$$

15. Solve the cubic equation by trial and error, factoring, or by using Mathematica or Excel:

$$x^3 + x^2 - 4x - 4 = 0.$$

16. Find the real root of the equation

$$x^2 - e^{-x} = 0.$$

17. Find the root of the equation

$$x - 2.00 \sin(x) = 0.$$

18. Find two positive roots of the equation

$$\ln(x) - 0.200x = 0.$$

19. Find the real roots of the equation

$$x^2 - 2.00 - \cos(x) = 0.$$

20. In the theory of black-body radiation, the following equation

$$x = 5(1 - e^{-x})$$

needs to be solved to find the wavelength of maximum spectral radiant emittance. The variable x is

$$x = \frac{hc}{\lambda_{max} k_B T},$$

where λ_{max} is the wavelength of maximum spectral radiant emittance, h is Planck's constant, c is the speed of light, k_B is Boltzmann's constant, and T is the absolute temperature. Solve the equation numerically for a value of x. Find the value of λ_{max} for $T = 6600$ K. In what region of the electromagnetic spectrum does this value lie?

21. Solve the simultaneous equations by hand, using the method of substitution:

$$x^2 + x + 3y = 15,$$
$$3x + 4y = 18.$$

[2] Henry F. Holtzclaw, Jr, William R. Robinson, and Jerone D. Odom, *General Chemistry*, 9th ed., p. 545, Heath, Lexington, MA, 1991.

Use Mathematica to check your result. Since the first equation is a quadratic equation, there will be two solution sets.

22. Stirling's approximation for $\ln(N!)$ is

$$\ln(N!) \approx \frac{1}{2}\ln(2\pi N) + N\ln(N) - N.$$

(a) Determine the validity of this approximation and of the less accurate version

$$\ln(N!) \approx N\ln(N) - N$$

for several values of N up to $N = 100$. Use a calculator, Excel, or Mathematica.

23. The Dieterici equation of state is

$$Pe^{a/V_m RT}(V_m - b) = RT,$$

where P is the pressure, T is the temperature, V_m is the molar volume, and R is the ideal gas constant. The constant parameters a and b have different values for different gases. For carbon dioxide, $a = 0.468$ Pa m^6 mol^{-2}, $b = 4.63 \times 10^{-5}$m^3 mol^{-1}. Without linearization, find the molar volume of carbon dioxide if $T = 298.15$ K and $P = 10.000$ atm $= 1.01325 \times 10^6$ Pa. Use Mathematica, Excel, or trial and error.

24. Determine which, if any, of the following sets of equations is inconsistent or linearly dependent. Draw a graph for each set of equations, showing both equations. Find the solution for any set that has a unique solution.

(a) $x + 3y = 4,$
$2x + 6y = 8.$

(b) $2x + 4y = 24,$
$x + 2y = 8.$

(c) $3x_1 + 4x_2 = 10,$
$4x_1 - 2x_2 = 6.$

25. Solve the set of equations using Mathematica or by hand with the method of substitution:

$$x^2 - 2xy + y^2 = 0,$$
$$2x + 3y = 5.$$

Chapter 6

Differential Calculus

Principal Facts and Ideas

- The derivative of a function is a measure of how rapidly the dependent variable changes with changes in the value of the independent variable.
- The derivative of a function is defined by a mathematical limit.
- The derivatives of many simple functions can be obtained by applying a few simple rules, either separately or in combination.
- A finite increment in a dependent variable, Δy, can sometimes be calculated approximately by use of the formula

$$\Delta y \approx \frac{dy}{dx}\Delta x.$$

- A relative minimum or maximum value of a variable $y(x)$ is found at a point where $dy/dx = 0$.
- The curvature of a function is defined by

$$K = \frac{d^2y/dx^2}{\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{3/2}}.$$

- At an inflection point, the curvature changes sign.

Objectives

After studying this chapter, you should be able to

- Obtain the formula for the derivative of any simple function without consulting a table;
- Sketch a rough graph of any fairly simple function and identify important features on the graph;
- Estimate a finite increment of a function using its derivative;
- Find maximum and minimum values of a function of one variable;
- Find inflection points of a function of one variable.

6.1 THE TANGENT LINE AND THE DERIVATIVE OF A FUNCTION

A curve representing a nonlinear function has a different direction (different steepness) at different points on the curve. The line tangent to the curve at a given point is a line that coincides with the curve at that point but does not cross it (except at an inflection point, which we discuss later). The tangent line has the same steepness as the curve at the given point.

Figure 6.1 shows the line that is tangent to the curve representing a function $y(x)$ at $x = x_1$. If the tangent line is represented by the formula

$$y = mx + b \tag{6.1}$$

the *slope* of the tangent line is equal to m. The figure includes a horizontal line intersecting the curve and the tangent line at $x = x_1$. In the figure, we have labeled another point at

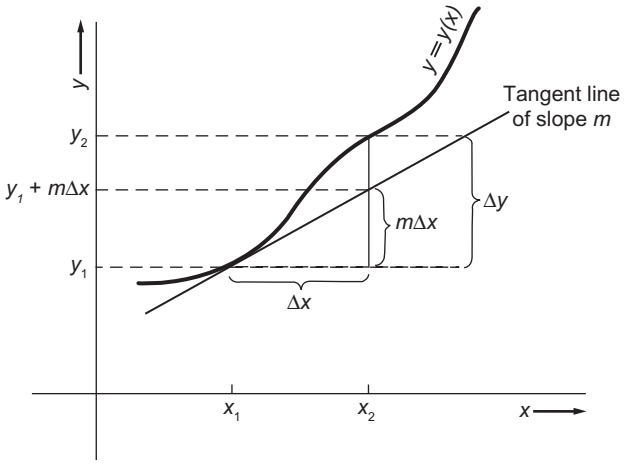


FIGURE 6.1 The curve representing the function $y = y(x)$ and its tangent line.

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00006-9

$x = x_2$. At this point the vertical distance from the horizontal line to the tangent line is given by

$$m(x_2 - x_1) = m\Delta x, \tag{6.2}$$

where we use a standard notation:

$$\Delta x = x_2 - x_1. \tag{6.3}$$

The distance $m\Delta x$ is not necessarily equal to the distance from the horizontal line to the curve, which is given by

$$y(x_2) - y(x_1) = y_2 - y_1 = \Delta y. \tag{6.4}$$

Exercise 6.1. Using graph paper plot the curve representing $y = \sin(x)$ for values of x lying between 0 and $\pi/2$ radians. Using a ruler, draw the tangent line at $x = \pi/4$. By drawing a right triangle on your graph and measuring its sides, find the slope of the tangent line.

There is a case in which the definition of the tangent line to a curve at a point x_1 is more complicated than in the case shown in Figure 6.1. In this case, the point x_1 lies between a region in which the curve is concave downward and a region in which the curve is concave upward. Such a point is called an *inflection point*. For such a point, we must consider tangent lines at points that are taken closer and closer to x_1. As we approach closer and closer to x_1 from either direction the tangent line will approach more and more closely to a line that is the tangent line at x_1. This line does cross the curve at the point that it shares with the curve. Figure 6.2 shows a graph of a function with an inflection point and the tangent line at this point.

6.1.1 The Derivative

We now discuss a mathematical way to construct the slope of the tangent line to a curve. Consider a nonlinear function $y = y(x)$ such as the function represented in Figure 6.1. If Δx is not too large, we can write as an approximation

$$\Delta y \approx m\Delta x, \tag{6.5}$$

where m is the slope of the tangent line. We divide both sides of Eq. (6.5) by Δx:

$$m \approx \frac{\Delta y}{\Delta x} = \frac{y(x_2) - y(x_1)}{x_2 - x_1} = \frac{y_2 - y_1}{x_2 - x_1}. \tag{6.6}$$

If the curve is smooth, this equation becomes a better approximation for m as Δx becomes smaller, and if we take the mathematical limit as $x_2 \to x_1$, it becomes exact if the limit exists:

$$\boxed{m = \lim_{x_2 \to x_1} \frac{y(x_2) - y(x_1)}{x_2 - x_1}}. \tag{6.7}$$

If the limit in Eq. (6.7) exists and has the same value when x_2 approaches x_1 from either side, it is called the *derivative* of the function at $x = x_1$. The derivative is denoted by the symbol dy/dx or the symbol y' or the symbol $y^{(1)}$ and is defined by

$$\frac{dy}{dx} = y' = \lim_{x_2 \to x_1} \frac{y(x_2) - y(x_1)}{x_2 - x_1} \quad \text{(definition)}. \tag{6.8}$$

If the derivative is to be evaluated at x_1, we would write $y'(x_1)$ or $(dy/dx)_{x_1}$.

If the limit in Eq. (6.7) does not exist at $x = x_1$ or if the limit has a different value when x_2 approaches x_1 from the two sides, the function is not *differentiable* at $x = x_1$. If $y(x)$ has a discontinuity at $x = x_1$, the function is not differentiable at that point. If the function has a cusp at $x = x_1$, the function is not differentiable at that point. A *cusp* corresponds to a "corner" or abrupt change in direction of a curve representing a function that is continuous at the point in question. The curve has different tangents immediately to the right and left of a cusp.

Figure 6.3 shows the graph of a function that has a step discontinuity at $x = b$ and a cusp at $x = a$. It is not

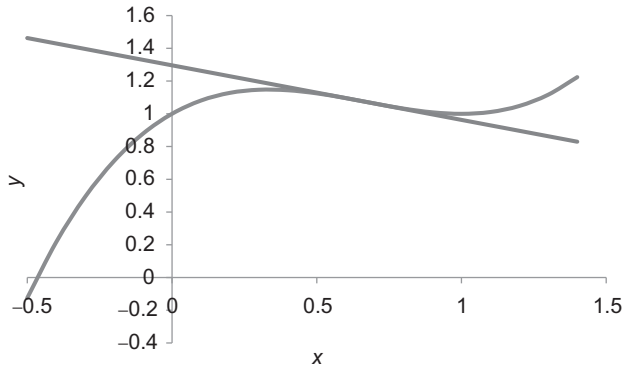


FIGURE 6.2 The curve representing the function $y(x) = x^3 - 2x^2 + x + 1$ and its tangent line at the inflection point.

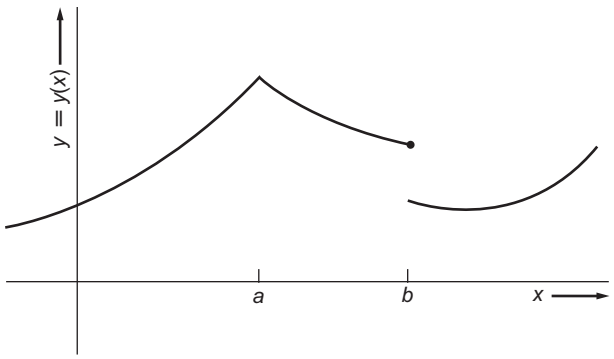


FIGURE 6.3 A function that is not differentiable at $x = a$ and at $y = b$.

differentiable at these points, although it is differentiable elsewhere in the region shown in the graph.

Example 6.1. Decide where the following functions are differentiable and where they are not differentiable:

(a) $y = |x|$.
This is differentiable everywhere except at $x = 0$, where there is a cusp.
(b) $y = \sqrt{x}$.

This function has real values for $x \geqslant 0$. It is differentiable for all positive values of$x$, but the limit does not exist at $x = 0$, so it is not differentiable at $x = 0$. The tangent to the curve at $x = 0$ is vertical.

Exercise 6.2. Decide where the following functions are differentiable:

(a) $y = \frac{1}{1-x}$.
(b) $y = x + 2\sqrt{x}$.
(c) $y = \tan(x)$.

6.1.2 Derivatives of Specific Functions

The derivatives of particular functions can be found from the definition of the derivative.

Example 6.2. Find the derivative of the function

$$y = ax^2.$$

Let $\Delta x = x_2 - x_1$ and let $\Delta y = y(x_2) - y(x_1) = y_2 - y_1$.

$$\begin{aligned}\Delta y &= ax_2^2 - ax_1^2 = a\left(x_1 + \Delta x\right)^2 - ax_1^2 \\ &= a\left[x_1^2 + 2x_1\Delta x + (\Delta x)^2\right] - ax_1^2 \\ &= 2ax_1\Delta x + (\Delta x)^2.\end{aligned}$$

$$\frac{\Delta y}{\Delta x} = 2ax_1 + \Delta x.$$

We now take the limit as $x_2 \to x_1 (\Delta x \to 0)$ The first term, $2ax_1$, is not affected. The second term, Δx, vanishes. Thus, if we use the symbol x instead of x_1

$$\frac{\mathrm{d}(ax^2)}{\mathrm{d}x} = \lim_{\Delta x \to 0} \frac{\Delta y}{\Delta x} = 2ax.$$

Figure 6.4 shows a graph of the function $y = ax^2$ and a graph of its derivative, $\mathrm{d}y/\mathrm{d}x = 2ax$.

The graph in Figure 6.4 exhibits some important general characteristics of derivatives:

- Where the function has a horizontal tangent line, the derivative is equal to zero.
- The derivative is positive in regions where the function increases as x increases.
- A positive derivative is larger when the tangent line is steeper.
- The derivative is negative where the function decreases as x increases.
- A negative derivative is more negative (has a larger magnitude) when the tangent line is steeper (has a negative slope of larger magnitude).

Example 6.3. Find the derivative of $y = x^n$ where n is an integer.

Using the binomial formula,

$$\begin{aligned}(x + \Delta x)^n &= x^n + \frac{n!}{(n-1)!1!}x^{n-1}\Delta x \\ &\quad + \frac{n!}{(n-2)!2!}x^{n-2}(\Delta x)^2 + \cdots,\end{aligned}$$

$$\begin{aligned}\frac{\mathrm{d}\left(x^n\right)}{\mathrm{d}x} &= \lim_{\Delta x \to 0} \frac{(x + \Delta x)^n - x^n}{\Delta x}, \\ &= \lim_{\Delta x \to 0} \frac{x^n + \frac{n!}{(n-1)!1!}x^{n-1}\Delta x + \frac{n!}{(n-2)!2!}x^{n-2}(\Delta x)^2 + \cdots - x^n}{\Delta x}, \\ &= \lim_{\Delta x \to 0} \left[\frac{n!}{(n-1)!1!}x^{n-1} + \frac{n!}{(n-2)!2!}x^{n-2}(\Delta x) + \cdots\right] = nx^{n-1}.\end{aligned}$$

Exercise 6.3. The exponential function can be represented by the following power series

$$e^{bx} = 1 + bx + \frac{1}{2!}b^2x^2 + \frac{1}{3!}b^3x^3 + \cdots + \frac{1}{n!}b^nx^n \cdots,$$

where the ellipsis $(\cdots)$ indicates that additional terms follow. The notation $n!$ stands for *n factorial,* such that $n! = n(n-1)(n-2)\cdots(3)(2)(1)$ for any positive integral value of n and $0! = 1$. Derive the expression for the derivative of e^{bx} from this series.

Table 6.1 gives the derivatives of several functions, where a, b, and c represent constants. Other derivatives are found in Appendix D.

Exercise 6.4. Draw rough graphs of several functions from Table 6.1. Below each graph, on the same sheet of paper, make a rough graph of the derivative of the same function.

6.2 DIFFERENTIALS

In Eq. (6.5), we wrote as an approximation

$$\Delta y \approx m\Delta x \tag{6.9}$$

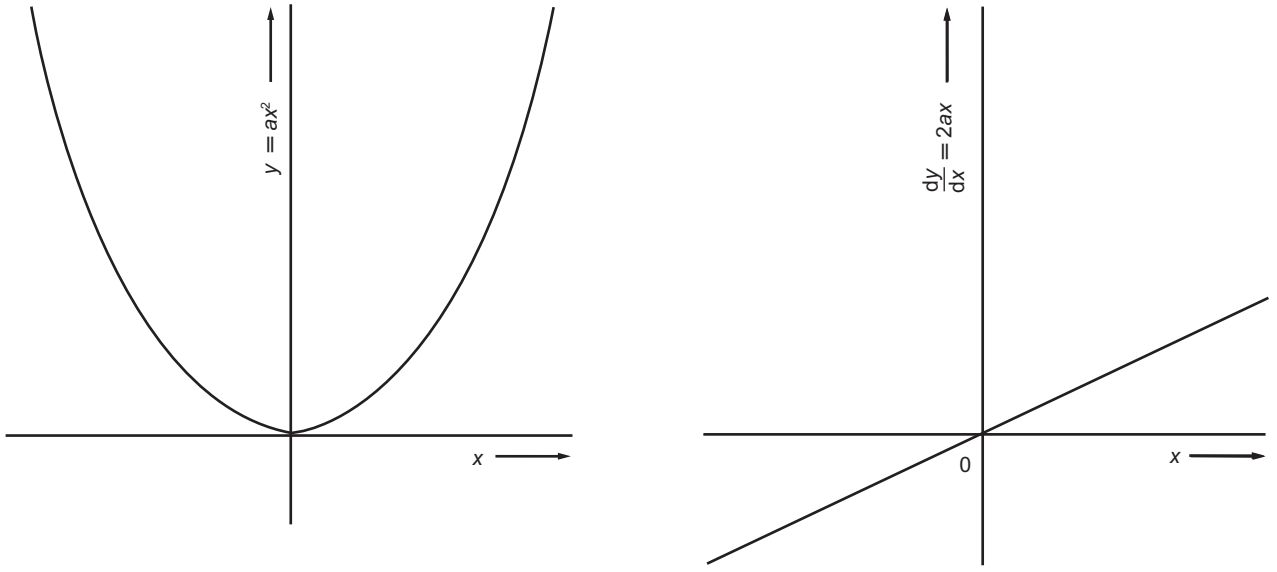


FIGURE 6.4 A graph of the function $y = ax^2$ and its derivative, $dy/dx = 2ax$.

TABLE 6.1 Some Elementary Functions and Their Derivatives

Function, $y = y(x)$	Derivative, $dy/dx = y'(x)$
ax^n	anx^{n-1}
ae^{bx}	abe^{bx}
a	0
$a\sin(bx)$	$ab\cos(x)$
$a\cos(bx)$	$-ab\sin(bx)$
$a\ln(x)$	a/x
$a\tan(x)$	

which is equivalent to

$$\Delta y \approx \left(\frac{dy}{dx}\right)\Delta x. \tag{6.10}$$

This approximation will generally be more nearly correct when Δx is made smaller.

Example 6.4. Using Eq. (6.10), estimate the change in the pressure of 1.000 mol of an ideal gas at 0 °C when its volume is changed from 22.414l to 21.414l.

An ideal gas obeys the equation

$$P = \frac{n\mathrm{RT}}{V},$$

so that if n and T are kept fixed, we can differentiate with respect to V:

$$\begin{aligned}\frac{dP}{dV} &= \frac{-n\mathrm{RT}}{V^2}\\ &= \frac{-(1.000\ \text{mol})(0.08206\ \text{l atm mol}^{-1}\ \text{K}^{-1})(273.15\ \text{K})}{(22.414\text{l})^2}\\ &= -0.0446\ \text{atm l}^{-1}.\end{aligned}$$

We can approximate an increment in P :

$$\begin{aligned}\Delta P &\approx \left(\frac{dP}{dV}\right)\Delta V = (-0.0446\ \text{atm l}^{-1})(-1.000\ \text{l})\\ &\approx 0.0446\ \text{atm}.\end{aligned}$$

We determine the accuracy of this result by calculating the actual change:

$$\begin{aligned}\Delta P &= P(21.414\ \text{l}) - P(22.414\ \text{l})\\ &= 1.0468\ \text{atm} - 1.0000\ \text{atm}\\ &= 0.0468\ \text{atm}.\end{aligned}$$

Our estimate was wrong by about 5%. If the change in volume had been 0.10 l, the error would have been about 0.5% . In this case it would have been easier to make the exact calculation.

Exercise 6.5. Assume that $y = 3.00x^2 - 4.00x + 10.00$. If $x = 4.000$ and $\Delta x = 0.500$, find the value of Δy using Eq. (6.10). Find the correct value of Δy.

Since Eq. (6.10) becomes more nearly exact as Δx is made smaller, we make it into an exact equation by making Δx become *infinitesimal*. That is, we make it smaller in magnitude than any nonzero quantity one might specify. In this limit, Δx becomes the *differential* of the independent variable, dx:

$$\boxed{dy = m\,dx = \left(\frac{dy}{dx}\right)dx}. \tag{6.11}$$

The infinitesimal quantity dy is the differential of the dependent variable. It represents the change in y that results from the infinitesimal increment dx in x. It is proportional to dx and to dy/dx. Since x is an independent variable, dx is arbitrary, or subject to our choice. Since y is a dependent variable, its differential dy is determined by dx, as specified by Eq. (6.11) and is not under our control once we have chosen a value for dx. Although Eq. (6.11) has the appearance of an equation in which the dx in the denominator is canceled by the dx in the denominator of a fraction, this is not a cancelation since dy/dx is the limit that a fraction approaches, which is not the same thing. In numerical calculations, differentials are not directly useful. Their use lies in the construction of formulas, especially through the process of integration, which we discuss in the next chapter.

6.3 SOME USEFUL DERIVATIVE IDENTITIES

We present some useful identities involving derivatives, which, together with the formulas for the derivatives of simple functions presented in Table 6.1, will enable you to obtain the derivative of almost any function that you will encounter in physical chemistry.

6.3.1 The Derivative of a Constant

If c is a constant,

$$\boxed{\frac{dc}{dx} = 0}. \tag{6.12}$$

From this follows the simple but important fact:

$$\boxed{\frac{d(y+c)}{dx} = \frac{dy}{dx}}. \tag{6.13}$$

If we add any constant to a function, we do not change its derivative.

6.3.2 The Derivative of a Function Times a Constant

If y is a function of x and c is a constant,

$$\boxed{\frac{d(cy)}{dx} = c\frac{dy}{dx}}. \tag{6.14}$$

6.3.3 The Derivative of a Product of Two Functions

If y and z are both functions of x,

$$\boxed{\frac{d(yz)}{dx} = y\frac{dz}{dx} + z\frac{dy}{dx}}. \tag{6.15}$$

6.3.4 The Derivative of the Sum of Two Functions

If y and z are both functions of x,

$$\boxed{\frac{d(y+z)}{dx} = \frac{dy}{dx} + \frac{dz}{dx}}. \tag{6.16}$$

6.3.5 The Derivative of the Difference of Two Functions

If y and z are both functions of x,

$$\boxed{\frac{d(y-z)}{dx} = \frac{dy}{dx} - \frac{dz}{dx}}. \tag{6.17}$$

6.3.6 The Derivative of the Quotient of Two Functions

If y and z are both functions of x, and z is not zero.

$$\boxed{\frac{d(y/z)}{dx} = \frac{z\left(\frac{dy}{dx}\right) - y\left(\frac{dz}{dx}\right)}{z^2}}. \tag{6.18}$$

An equivalent result can be obtained by considering y/z to be a product of y and $1/z$ and using Eq. (6.15),

$$\boxed{\frac{d}{dx}\left(y\frac{1}{z}\right) = \frac{1}{z}\frac{dy}{dx} - y\frac{1}{z^2}\frac{dz}{dx}}. \tag{6.19}$$

Many people think that Eq. (6.19) is more convenient to use than Eq. (6.18).

6.3.7 The Derivative of a Function of a Function (the Chain Rule)

If u is a differentiable function of x, and f is a differentiable function of u,

$$\boxed{\frac{df}{dx} = \frac{df}{du}\frac{du}{dx}}. \tag{6.20}$$

The function f is sometimes referred to as a *composite function*. It is indirectly a function of x because x is a function of u. Specifying a value of x specifies a value of u,

which specifies a value of f. This can be communicated by the notation

$$f(x) = f[u(x)]. \tag{6.21}$$

Here we have used the same letter for the function f whether it is expressed as a function of u or of x.

We now illustrate how these facts about derivatives can be used to obtain formulas for the derivatives of various functions.

Example 6.5. Find the derivative of $\tan(ax)$ by using the formulas for the derivatives of the sine and cosine.

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}x}\tan(ax) &= \frac{\mathrm{d}}{\mathrm{d}x}\left[\frac{\sin(ax)}{\cos(ax)}\right] \\ &= \frac{\cos(ax)a\cos(ax) + \sin(ax)a\sin(ax)}{\cos^2(ax)} \\ &= a\left[\frac{\cos^2(ax) + \sin^2(ax)}{\cos^2(ax)}\right] = \frac{a}{\cos^2(ax)} \\ &= a\sec^2(ax).\end{aligned}$$

We have used several trigonometric identities.

Example 6.6. Find $\mathrm{d}P/\mathrm{d}T$ if $P(T) = ke^{-Q/T}$.

Let $u = -Q/T$. From the chain rule,

$$\begin{aligned}\frac{\mathrm{d}P}{\mathrm{d}T} &= \frac{\mathrm{d}P}{\mathrm{d}u}\frac{\mathrm{d}u}{\mathrm{d}T} = ke^{u}\frac{Q}{T^2} \\ &= ke^{-Q/T}\left(\frac{Q}{T^2}\right).\end{aligned}$$

Exercise 6.6. Find the following derivatives. All letters stand for constants except for the dependent and independent variables indicated:

(a) $\dfrac{\mathrm{d}y}{\mathrm{d}x}$, where $y = (ax^2 + bx + c)^{-3/2}$.

(b) $\dfrac{\mathrm{d}\ln(P)}{\mathrm{d}T}$, where $P = ke^{-Q/T}$.

(c) $\dfrac{\mathrm{d}y}{\mathrm{d}x}$, where $y = a\cos(bx^3)$.

6.4 NEWTON'S METHOD

This method, which is also called the *Newton-Raphson method*, is an *iterative procedure* for obtaining a numerical solution to an algebraic equation. An iterative procedure is one that is repeated until the desired degree of accuracy is attained. The procedure is illustrated in Figure 6.5. We assume that we have an equation written in the form

$$f(x) = 0, \tag{6.22}$$

where $f(x)$ is a differentiable function.

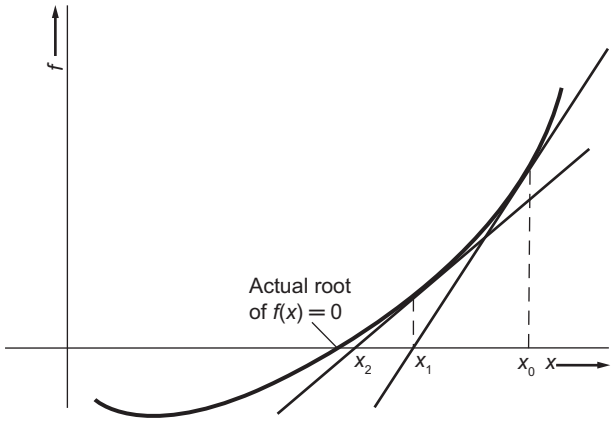


FIGURE 6.5 Graph to illustrate Newton's method.

The process is as follows:

Step 1. Guess at a value, x_0, which is not too far from the actual root. A rough graph of the function $f(x)$ can help you to choose a good value for x_0.

Step 2. Find the value of $f(x)$ and the value of $\mathrm{d}f/\mathrm{d}x$ at $x = x_0$.

Step 3. Using the value of $f(x)$ and $\mathrm{d}f/\mathrm{d}x$, find the value of x at which the tangent line to the curve at $x = x_0$ crosses the axis. This value of x, which we call x_1, is our next approximation to the root. It is given by

$$x_1 = x_0 - \frac{f(x_0)}{f^{(1)}(x_0)}, \tag{6.23}$$

where we use the notation

$$f^{(1)}(x_0) = \left(\frac{\mathrm{d}f}{\mathrm{d}x}\right)_{x=x_0}. \tag{6.24}$$

or the derivative evaluated at $x = x_0$.

Step 4. Repeat the process until you are satisfied with the accuracy obtained. The nth approximation is given by

$$\boxed{x_n = x_{n-1} - \frac{f(x_{n-1})}{f^{(1)}(x_{n-1})}}. \tag{6.25}$$

Example 6.7. Using Newton's method, find the positive root of the equation

$$e^{-x} - x^2 = 0.$$

A graph indicates that the root is near $x = 0.7$. Choose $x_0 = 0.7000$

$$\begin{aligned}f(0.7000) &= 0.0065853, \\ \frac{\mathrm{d}f}{\mathrm{d}x} &= f^{(1)} = -e^{-x} - 2x,\end{aligned}$$

$$\left.\frac{df}{dx}\right|_{x=0.7} = f^{(1)}(0.7000) = -1.8966,$$

$$x_1 = 0.7000 - \frac{0.0065853}{-1.8966} = 0.70347,$$

$$f(x_1) = f(0.70347) = -9.01115 \times 10^{-6},$$

$$\left.\frac{df}{dx}\right|_{x=0.70347} = f^{(1)}(0.70347) = -2.4069,$$

$$x_2 = 0.70347 - \frac{-9.01115 \times 10^{-6}}{-2.4069} = 0.70347.$$

The second iteration produces the same result as the first, so we stop at this point and assert that the root is at $x = 0.70347$ To five significant digits, this is the correct answer.

You must decide when to stop the iteration. If the graph of the function $f(x)$ crosses the x axis at the root, you can probably stop when the difference between x_n and x_{n+1} is smaller than the error you can tolerate. However, if the curve becomes tangent to the x axis at the root, the method may converge very slowly. It may be necessary to pick another trial root on the other side of the root and to compare the two results. Another possibility is to take the derivative of the function, set that equal to zero, and solve for that root, since the first derivative changes sign if the function is tangent to the x axis.

You must be careful with your choice of x_0. If there are several roots, a poor choice of x_0 can make the method converge to the wrong root. If your choice of x_0 is near a local maximum or a local minimum, the first application of the procedure might give a value of x_1 that is nowhere near the desired root, and the procedure might lead you to a root other than the one you want. These kinds of problems can be troublesome when you are using a computer to do the iterations, because you might not see the values of x_1, x_2, and so on, until the program has finished execution. Remember the *first maxim of computing*: "Garbage in, garbage out." Carrying out an approximate graphical solution before you start is a good idea.

Exercise 6.7. Carry out Newton's method by hand to find the smallest positive root of the equation

$$1.000x^2 - 5.000x + 1.000 = 0.$$

6.5 HIGHER-ORDER DERIVATIVES

The derivative of the derivative of a function is called a *second derivative* of that function and the derivative of a second derivative is called a *third derivative*, and so on. A function that possesses all of its derivatives is said to be *analytic*.

For the second derivative, we use the notation d^2f/dx^2 or $f^{(2)}$

$$\frac{d^2y}{dx^2} = f^{(2)} = \frac{dd}{dx}\left(\frac{dy}{dx}\right) \tag{6.26}$$

and for the third derivative we use the notation

$$\frac{d^3y}{dx^3} = f^{(3)} = \frac{d}{dx}\left(\frac{d^2y}{dx^2}\right). \tag{6.27}$$

The nth-order derivative is denoted by

$$\frac{d^ny}{dx^n} = f^{(n)} = \frac{d}{dx}\left(\frac{d^{n-1}y}{dx^{n-1}}\right). \tag{6.28}$$

The notation $y''(x)$ is commonly used for the second derivative. The third and higher-order derivatives are sometimes denoted by a lower-case Roman numeral superscript in parentheses, as $y^{(iii)}, y^{(iv)}$, and so on.

Example 6.8. Find d^2y/dx^2 if $y = a \sin(bx)$.

$$\frac{d^2[a \sin(bx)]}{dx^2} = \frac{d}{dx}[ab \cos(bx)] = -ab^2 \sin(bx).$$

The result of this example is sometimes useful: the sine is proportional to the negative of its second derivative. The cosine has the same behavior. The exponential function is proportional to all of its derivatives.

Exercise 6.8. Find the second and third derivatives of the following functions. Treat all symbols except for the specified independent variable as constants:

(a) $y = y(x) = ax^n$.
(b) $y = y(x) = ae^{bx}$.

Figure 6.6 shows a rough graph of a function, its first derivative, and its second derivative in the interval $a < x < g$.

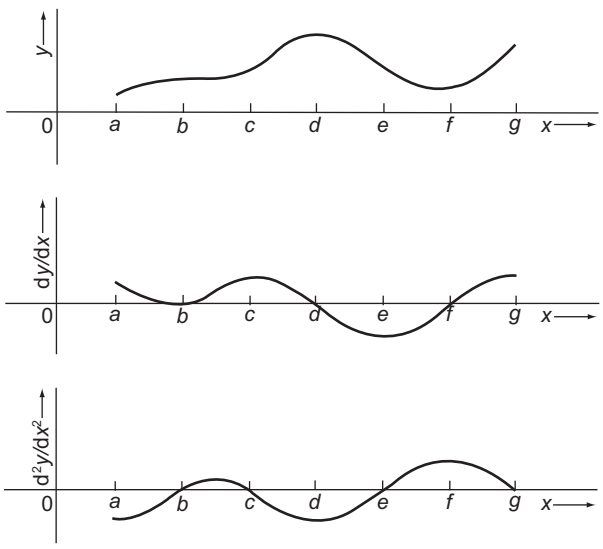


FIGURE 6.6 A function and its first and second derivatives.

6.5.1 The Curvature of a Function

The second derivative of a function provides a measure of the curvature of the curve representing that function. For any function that possesses a first and a second derivative, the *curvature K* is defined by

$$K = \frac{d^2y/dx^2}{\left[1 + \left(dy/dx\right)^2\right]^{3/2}} \quad \text{(definition)}. \tag{6.29}$$

If the curve representing the function is concave downward, the curvature is negative, and if the curve is concave upward, the curvature is positive. The magnitude of the curvature at a given point is equal to the reciprocal of the radius of the circle that fits the curve at that point. If the graph of the function is more sharply curved, the radius of the circle is smaller and the magnitude of the curvature is larger. Since the denominator in this expression is always positive, the curvature has the same sign as the second derivative. At a point where the first derivative is zero, the curvature is equal to the second derivative.

Example 6.9. Find the curvature of the function $y = x^2$ at $x = 0$ and at $x = 2$.

$$\frac{d^2y}{dx^2} = \frac{d}{dx}(2x) = 2,$$

$$K = \frac{2}{\left(1 + 4x^2\right)^{3/2}} = \begin{cases} 2 & \text{at } x = 0 \\ 0.0285 & \text{at } x = 2 \end{cases}$$

Exercise 6.9. Find the curvature of the function $y = \cos(x)$ at $x = 0$ and at $x = \pi/2$.

6.6 MAXIMUM–MINIMUM PROBLEMS

The *minimum value* of a function means the most negative value of the function. The *maximum value* means the most positive value of the function. Either a maximum or a minimum is called an *extremum*. We now state the fact that enables us to find maximum and minimum values of a differentiable function in a given interval: *The minimum or maximum value of a differentiable function in an interval occurs at an end of the interval, at a cusp, at a discontinuity, or at a point where the first derivative of the function vanishes.* At a point where the first derivative vanishes, we have either a *relative minimum* or a *relative maximum*. At a *relative minimum*, also called a *local minimum*. the function has a smaller value than at any other point in the immediate vicinity. At a relative maximum or a *local maximum*, the function has a larger value than at any other point in the immediate vicinity. A maximum or minimum value is also called an *extremum*.

We illustrate the process of finding the maximum and minimum values of a function depicted in Figure 6.6. In the interval shown there are three points at which the first derivative vanishes, labeled b, d, and f. The maximum value of the function could occur at one of these three points or at one of the ends of the interval, labeled a and g. The first derivative also vanishes at point b, but this is an *inflection point* with a horizontal tangent line. An inflection point cannot be either a relative maximum or a relative minimum since the function is larger on one side of the point and smaller on the other side. To find the maximum value we compare the value of the function at point d and at the ends of the interval. Inspection of the graph indicates that point d is the *absolute maximum* of the function in the interval shown. Inspection of the graph indicates that the left end of the interval (point a) is the *absolute minimum*.

We summarize this procedure.

1. Find all the points in the interval at which the first derivative vanishes.
2. Evaluate the function at all of these points, at any cusp or discontinuity, and at the ends of the interval. The largest value in the list is the maximum value and the smallest value is the minimum.

You can distinguish relative minima, relative maxima, and inflection points from each other by finding the sign of the curvature, which is equal to the second derivative at a point with zero first derivative. At a relative minimum, the second derivative is positive. At a relative maximum, the second derivative is negative. At an inflection point with horizontal tangent line, the second derivative vanishes.

Example 6.10. Find the maximum and minimum values of the function

$$y = x^2 - 4x + 6$$

in the interval $0 < x < 5$.

The first derivative is

$$3\frac{dy}{dx} = 2x - 4.$$

There is only one point at which $dy/dx = 0$. Call it $x_{\min}$.

$$2x_{\min} - 4 = 0 \quad \text{or} \quad x_{\min} = 2.$$

This is a relative minimum, as can be seen from the second derivative, which is positive for all values of x:

$$\frac{d^2y}{dx^2} = 2.$$

We evaluate the function at the ends of the interval and at $x = x_{\min}$:

$$\begin{aligned} y(0) &= 6, \\ y(x_{\min}) &= y(2) = 2, \\ y(5) &= 11. \end{aligned}$$

The maximum value of the function is at $x = 5$, the end of the interval. The minimum value is at the relative minimum at $x = 2$.

Example 6.11. Find the maximum and minimum values of the function $f = 1 - |x|$ in the interval $-1 \leqslant x \leqslant 1$.

There is a cusp at $x = 0$, where $f(0) = 1$. The first derivative does not vanish in the region. The function is nonzero in the entire interval and vanishes at the ends of the interval. The maximum value is at the cusp at $x = 0$, and the minimum value is at both ends of the interval, at $x = \pm 1$.

Exercise 6.10. For the interval $-10 \leqslant x \leqslant 10$, find the maximum and minimum values of

$$y = -1.000x^3 + 3.000x^2 - 3.000x + 8.000.$$

An inflection point does not have to correspond to a horizontal tangent line.

Example 6.12. Locate the inflection point in the function

$$y = x^3 - 2x^2 + x + 1.$$

The first derivative is

$$\frac{\mathrm{d}y}{\mathrm{d}x} = 3x^2 - 4x + 1$$

and the second derivative is

$$\frac{\mathrm{d}^2y}{\mathrm{d}x^2} = 6x - 4.$$

The second derivative vanishes at $x = 2/3$, which is the inflection point. At this point, the function is equal to

$$y(2/3) = \frac{8}{27} - 2\left(\frac{4}{9}\right) + \frac{2}{3} + 1 = 0.62963.$$

This inflection point does not correspond to a horizontal tangent line. The first derivative at this point is equal to

$$\frac{\mathrm{d}y}{\mathrm{d}x} = 3\left(\frac{4}{9}\right) - 4\left(\frac{2}{3}\right) + 1 = -\frac{1}{3}.$$

Exercise 6.11. Find the inflection points for the function $y = \sin(x)$.

6.7 LIMITING VALUES OF FUNCTIONS

The limit of y as x approaches a is denoted by

$$\lim_{x \to a} [y(x)] \tag{6.30}$$

and is defined as the value that y approaches ever more closely as x approaches ever more closely to a, if such a number exists. The number a is not required to be finite, and a limit such as

$$\lim_{x \to \infty} y(x)] \tag{6.31}$$

exists if $y(x)$ approaches more closely to some fixed value as x is made larger and larger without bound. An example of a limit that does exist as x approaches infinity is

$$\lim_{x \to \infty} (1 - e^{-x}) = 1. \tag{6.32}$$

A limit that does not exist is

$$\lim_{x \to \infty} [\sin(x)]. \tag{6.33}$$

The sine function continues to oscillate between -1 and 1 as x becomes larger and larger. Another limit that does not exist is

$$\lim_{x \to \infty} e^x = \infty. \tag{6.34}$$

The exponential function becomes larger and larger without bound as its argument is made larger and larger.

In some cases it matters whether the limit is approached from the right or from the left. An example of a limit that does not exist is

$$\lim_{x \to a} \left(\frac{1}{x - a}\right). \tag{6.35}$$

As x approaches closer to a, $1/(x - a)$ becomes larger without bound if $x$approaches a from the right (from values larger than a) and $1/(x - a)$ becomes more negative without bound if x approaches a from the left.

Example 6.13. Decide which of the following limits exists and find the values of those that do exist:

(a) $\lim_{x \to 0} \left(1 - e^{-x}\right)$.
As x approaches 0 from the right, the term e^{-x} smoothly approaches unity, so the function approaches zero. As x approaches 0 from the left, the term e^{-x} smoothly approaches unity, so the function approaches zero. The limiting value of the function is zero.

(b) $\lim_{x \to \infty} \left(e^{-x^2}\right)$.

As x becomes larger and larger, the function approaches zero, so the limiting value is zero.

Exercise 6.12. Decide which of the following limits exists and find the values of those that do exist:

(a) $\lim_{x \to \pi/2} [x \tan(x)]$.

(b) $\lim_{x \to 0} [\ln(x)]$.

6.8 L'HÔPITAL'S RULE

Sometimes a limit exists but cannot be evaluated by substituting into the expression the limiting value of the independent variable. For example, if we try to determine the limit

$$\lim_{x\to 0}\left[\frac{\sin(x)}{x}\right] \tag{6.36}$$

we find that as we approach $x = 0$ both the numerator and denominator of the expression approach zero. If an expression appears to approach 0/0, it might approach 0, it might approach a finite constant of either sign, or it might diverge in either direction (approach $-\infty$ or $+\infty$). The same is true if the limit appears to approach ∞/∞ or $0\times\infty$.

The [1] *rule of l'Hôpital* provides a way to determine the limit in such cases. This rule can be stated: *If the numerator and denominator of a quotient both approach zero or both approach infinity in some limit, the limit of the quotient is equal to the limit of the quotient of the derivatives of the numerator and denominator if this limit exists.*

$$\boxed{\lim_{x\to a}\left[\frac{f(x)}{g(x)}\right] = \lim_{x\to a}\left[\frac{\mathrm{d}f/\mathrm{d}x}{\mathrm{d}g/\mathrm{d}x}\right] = \lim_{x\to a}\left[\frac{f'(x)}{g'(x)}\right]}. \tag{6.37}$$

Example 6.14. Find the value of the limit in Eq. (6.36) by use of l'Hôpital's rule.

$$\lim_{x\to 0}\left[\frac{\sin(x)}{x}\right] = \lim_{x\to 0}\left[\frac{\mathrm{d}\sin(x)/\mathrm{d}x}{\mathrm{d}x/\mathrm{d}x}\right] = \lim_{x\to 0}\left[\frac{\cos(x)}{1}\right] = 1.$$

l'Hôpital's rule does not necessarily give the correct limit if it is applied to a case in which the limit does not appear to approach 0/0 or ∞/∞ or $0\times\infty$. As one author put it: "As a rule of thumb, l'Hôpital's rule applies when you need it, and not apply when you do not need it."

Exercise 6.13. Find the value of the limit:

$$\lim_{x\to 0}\left[\frac{\tan(x)}{x}\right].$$

If a limiting expression appears to approach $0\times\infty$, it can be put into a form that appears to approach 0/0 or ∞/∞ by using the reciprocal of one factor. In addition the rule must sometimes be applied more than once in order to find the value of the limit.

Example 6.15. Find the limit

$$\lim_{x\to\infty}\left(x^3e^{-x}\right)$$

We apply l'Hôpital's rule three times

$$\lim_{x\to\infty}\left(x^3e^{-x}\right) = \lim_{x\to\infty}\left(\frac{x^3}{e^x}\right) = \lim_{x\to\infty}\left(\frac{3x^2}{e^x}\right) = \lim_{x\to\infty}\left(\frac{6x}{e^x}\right) = \lim_{x\to\infty}\left(\frac{6}{e^x}\right) = 0.$$

By applying l'Hôpital's rule n times, we can show that

$$\lim_{x\to\infty}\left(x^ne^{-x}\right) = 0 \tag{6.38}$$

for any finite value of n. The exponential function e^{-x} approaches zero so rapidly that it overwhelms any finite power of x in the limit that x becomes large.

Exercise 6.14. Investigate the limit

$$\lim_{x\to\infty}\left(x^{-n}e^{x}\right)$$

for any finite value of n.

Example 6.16. Find the limit

$$\lim_{x\to\infty}\left(\frac{\ln(x)}{x}\right),$$

$$\lim_{x\to\infty}\left(\frac{\ln(x)}{x}\right) = \lim_{x\to\infty}\left(\frac{1/x}{1}\right) = 0.$$

Exercise 6.15. Find the limit

$$\lim_{x\to\infty}\left[\frac{\ln(x)}{\sqrt{x}}\right].$$

l'Hôpital's rule is useful in some limits that occur in physical chemistry.[2]

Example 6.17. A collection of N harmonic oscillators at thermal equilibrium at absolute temperature $T$is shown by statistical mechanics to have the thermodynamic energy

$$U = \frac{Nh\nu}{e^{h\nu/k_\mathrm{B}T} - 1},$$

where k_B is Boltzmann's constant, h is Planck's constant, T is the absolute temperature, and ν is the vibrational frequency. Find the limit of U as $\nu \to 0$. Find the limit of U as $T \to 0$.

[1] The rule is named after the 17th-century French mathematician Guillaume de l'Hôpital, but the rule was likely discovered by the Swiss mathematician Johann Bernoulli.

[2] Missen, Ronald W., "Applications of the l'Hôpital-Bernoulli Rule in Chemical Systems", *J. Chem. Educ*. **54**, 448 (1977).

As $\nu \to 0$, both the numerator and denominator approach zero. We apply l'Hôpital's rule. The derivative of the numerator with respect to ν is equal to Nh. The derivative of the denominator is

$$\frac{\mathrm{d}}{\mathrm{d}\nu}\left(e^{h\nu/k_\mathrm{B}T}-1\right)=\frac{h}{k_\mathrm{B}T}e^{h\nu/k_\mathrm{B}T}.$$

As $\nu \to 0$, this derivative approaches $h/k_\mathrm{B}T$.

$$\lim_{\nu\to 0} U=\frac{Nh}{h/k_\mathrm{B}T}=k_\mathrm{B}T.$$

As $T \to 0$ there is no need to apply l'Hôpital's rule. The numerator remains constant, but the denominator becomes large without bound so that

$$\lim_{T\to 0} U=0.$$

Exercise 6.16. Find the limit

$$\lim_{\nu\to\infty}\left(\frac{Nh\nu}{e^{h\nu/k_\mathrm{B}T}-1}\right).$$

Problems

1. The sine and cosine functions are represented by the two series

$$\sin(x)=x-\frac{x^3}{3!}+\frac{x^5}{5!}-\frac{x^7}{7!}+\cdots,$$
$$\cos(x)=1-\frac{x^2}{2!}+\frac{x^4}{4!}-\frac{4^6}{6!}+\cdots.$$

Differentiate each series to show that

$$\frac{\mathrm{d}\sin(x)}{\mathrm{d}x}=\cos(x)$$

and

$$\frac{\mathrm{d}\cos(x)}{\mathrm{d}x}=-\sin(x).$$

2. The natural logarithm of $1+x$ is represented by the series

$$\ln(1+x)=x-\frac{x^2}{2}+\frac{x^3}{3}-\frac{x^4}{4}\cdots$$
(valid for $x^2<1$ and $x=1$).

Use the identity

$$\frac{\mathrm{d}\ln(x)}{\mathrm{d}x}=\frac{1}{x}$$

to find a series to represent $1/(1+x)$.

3. Use the definition of the derivative to derive the formula

$$\frac{\mathrm{d}(yz)}{\mathrm{d}x}=y\frac{\mathrm{d}z}{\mathrm{d}x}+z\frac{\mathrm{d}y}{\mathrm{d}x},$$

where y and z are both functions of x.

4. The number of atoms of a radioactive substance at time t is given by

$$N(t)=N_\mathrm{o}e^{-t/\tau},$$

where N_o is the initial number of atoms and τ is the relaxation time. For $^{14}\mathrm{C}, \tau = 8320y$. Calculate the fraction of an initial sample of $^{14}\mathrm{C}$ that remains after 15.00 years, using Eq. (6.10). Calculate the correct fraction and compare it with your first answer.

5. Find the first and second derivatives of the following functions:

(a) $P=P(V_\mathrm{m})=\mathrm{RT}(1/V_\mathrm{m}+B/V_\mathrm{m}^2+C/V_\mathrm{m}^3)$ where R, B, and C are constants.
(b) $G=G(x)=G^\circ+\mathrm{RT}x\ln(x)+\mathrm{RT}(1-x)\ln(1-x)$, where G°, R, and T are constants.
(c) $y=y(x)=a\ln(x^{1/3})$, where a is a constant.

6. Find the first and second derivatives of the following functions:

(a) $y=y(x)=3x^3\ln(x)$.
(b) $y=y(x)=1/(c-x^2)$, where c is a constant.
(c) $y=y(x)=ce^{-a\cos(bx)}$, where a, b, and c are constants.

7. Find the first and second derivatives of the following functions:

(a) $y=(1/x)(1/(1+x))$.
(b) $f=f(v)=ce^{-mv^2/(2kT)}$ where m, c, k, and T are constants.

8. Find the first and second derivatives of the following functions:

(a) $y=3\sin^2(2x)=3\sin(2x)^2$.
(b) $y=a_0+a_1x+a_2x^2+a_3x^3+a_4x^4+a_5x^5$, where a_0, a_1, and so on are constants.
(c) $y=a\cos(e^{-bx})$, where a and b are constants.

9. Find the second and third derivatives of the following functions. Treat all symbols except for the specified independent variable as constants:

(a) $v_\mathrm{rms}=v_\mathrm{rms}(T)=\sqrt{\frac{3\mathrm{RT}}{M}}$.
(b) $P=P(V)=\dfrac{nRT}{(V-nb)}-\dfrac{an^2}{V^2}$.

10. Find the following derivatives and evaluate them at the points indicated:

(a) $(dy/dx)_{x=0}$ if $y = \sin(bx)$, where b is a constant.
(b) $(df/dt)_{t=0}$ if $f = Ae^{-kt}$, where A and k are constants.

11. Find the following derivatives and evaluate them at the points indicated:

(a) $(dy/dx)_{x=1}$, if $y = \left(ax^3 + bx^2 + cx + 1\right)^{-1/2}$, where a,b, and c are constants.
(b) $\left(d^2y/dx^2\right)_{x=0}$, if $y = ae^{-bx}$, where a and b are constants.

12. Find the following derivatives:

(a) $\dfrac{d(yz)}{dx}$, where $y = ax^2$, $z = \sin(bx)$.

(b) $\dfrac{dP}{dV}$, where $P = \dfrac{nRT}{(V - nb)} - \dfrac{an^2}{V^2}$.

(c) $\dfrac{d\eta}{d\lambda}$, where $\eta = \dfrac{2\pi hc^2}{\lambda^5\left(e^{hc/\lambda kT} - 1\right)}$.

13. Find a formula for the curvature of the function:

$$P(V) = \frac{nRT}{V - nb} - \frac{an^2}{V^2},$$

where n,R,a,b, and T are constants

14. The volume of a cube is given by

$$V = V(a) = a^3,$$

where a is the length of a side. Estimate the percent error in the volume if a 1.00% error is made in measuring the length, using the formula

$$\Delta V \approx \left(\frac{dV}{da}\right)\Delta a.$$

Check the accuracy of this estimate by comparing $V(a)$ and $V(1.0100a)$.

15. Draw a rough graph of the function

$$y = y(x) = e^{-|x|}.$$

Is the function differentiable at $x = 0$? Draw a rough graph of the derivative of the function.

16. Draw a rough graph of the function

$$y = y(x) = \sin(|x|).$$

Is the function differentiable at $x = 0$? Draw a rough graph of the derivative of the function.

17. Draw a rough graph of the function

$$y = y(x) = \cos(|x|).$$

Is the function differentiable at $x = 0$? Draw a rough graph of the derivative of the function.

18. Show that the function $\psi = \psi(x) = A\sin(kx)$ satisfies the equation

$$\frac{d^2\psi}{dx^2} = -k^2\psi,$$

if A and k are constants.

19. Show that the function $\psi = \psi(x)\cos(kx)$ satisfies the equation

$$\frac{d^2\psi}{dx^2} = -k^2\psi,$$

if A and k are constants.

20. Draw rough graphs of the third and fourth derivatives of the function whose graph is given in Figure 6.6.

21. The mean molar Gibbs energy of a mixture of two *enantiomorphs* (optical isomers of the same substance) is given at a constant temperature T by

$$G_m = G_m(x) = G_m{}^\circ + RTx\ln(x) + RT(1 - x)\ln(1 - x),$$

where x is the mole fraction of one of them. $G_m{}^\circ$ is a constant, R is the ideal gas constant, and T is the constant temperature. What is the concentration of each enantiomorph when G has its minimum value? What is the maximum value of G in the interval $0 \leqslant x \leqslant 1$?

22. **(a)** A rancher wants to enclose a rectangular part of a large pasture so that 1.000 km^2 is enclosed with the minimum amount of fence. Find the dimensions of the rectangle that he should choose. The area is

$$A = xy$$

but A is fixed at 1.000 km^2, so that $y = A/x$.

(b) The rancher now decides that the fenced area must lie along a road and finds that the fence costs \$20.00 per meter along the road and \$10.00 per meter along the other edges. Find the dimensions of the rectangle that would minimize the cost of the fence.

23. The sum of two nonnegative numbers is 100. Find their values if their product plus twice the square of the first is to be a maximum.

24. A cylindrical tank in a chemical factory is to contain 2.000 m^3 of a corrosive liquid. Because of the cost of the material, it is desirable to minimize the area of the tank. Find the optimum radius and height and find the resulting area.

25. Find the following limits:

(a) $\lim_{x\to\infty}[\ln(x)/x^2]$.
(b) $\lim_{x\to 3}\left[(x^3-27)/(x^2-9)\right]$.
(c) $\lim_{x\to\infty}[x\ln\left(\frac{1}{1+x}\right)]$.

26. Find the following limits:

(a) $\lim_{x\to 0^+}\left[\frac{\ln(1+x)}{\sin(x)}\right]$.
(b) $\lim_{x\to 0^+}[\sin(x)\ln(x)]$.

27. Find the following limits:

(a) $\lim_{x\to\infty}\left(e^{-x^2}/e^{-x}\right)$.
(b) $\lim_{x\to 0}\left[x^2/(1-\cos(2x))\right]$.
(c) $\lim_{x\to\pi}[\sin(x)/\sin(3x/2)]$.

28. Find the maximum and minimum values of the function

$$y = x^3 + 4x^2 - 10x$$

in the interval $-5 < x < 5$.

29. If a hydrogen atom is in a $2s$ state, the probability of finding the electron at a distance r from the nucleus is proportional to $4\pi r^2\psi_{2s}^2$ where ψ represents the orbital (wave function):

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0},$$

where a_0 is a constant known as the Bohr radius, equal to 0.529×10^{-10}m.

(a) Locate the maxima and minima of ψ_{2s}.
(b) Draw a rough graph of ψ_{2s}.
(c) Locate the maxima and minima of ψ_{2s}^2.
(d) Draw a rough graph of ψ_{2s}^2.
(e) Locate the maxima and minima of $4\pi r^2\psi_{2s}^2$.
(f) Draw a rough graph of $4\pi r^2\psi_{2s}^2$.

30. The probability that a molecule in a gas will have a speed v is proportional to the function

$$f_v(v) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2\exp\left(\frac{-mv^2}{2k_B T}\right),$$

where m is the mass of the molecule, k_B is Boltzmann's constant, and T is the temperature on the Kelvin scale. The most probable speed is the speed for which this function is at a maximum. Find the expression for the most probable speed and find its value for nitrogen molecules at $T = 298$ K. Remember to use the mass of a molecule, not the mass of a mole.

31. According to the Planck theory of black-body radiation, the *radiant spectral emittance* is given by the formula

$$\eta = \eta(\lambda) = \frac{2\pi hc^2}{\lambda^5(e^{hc/\lambda,k_B T}-1)}$$

where λ is the wavelength of the radiation, h is Planck's constant, k_B is Boltzmann's constant, c is the speed of light, and T is the temperature on the Kelvin scale. Treat T as a constant and find an equation that gives the wavelength of maximum emittance.

32. The thermodynamic energy of a collection of N harmonic oscillators (approximate representations of molecular vibrations) is given by

$$U = \frac{Nh\nu}{e^{h\nu/k_B T}-1}. \tag{6.39}$$

(a) Draw a rough sketch of the thermodynamic energy as a function of T.
(b) The heat capacity of this system is given by

$$C = \frac{dU}{dT}.$$

Show that the heat capacity is given by

$$C = Nk_B\left(\frac{h\nu}{k_B T}\right)^2\frac{e^{h\nu/k_B T}}{(e^{h\nu/k_B T}-1)^2}.$$

(c) Find the limit of the heat capacity as $T\to 0$ and as $T\to\infty$. Note that the limit as $T\to\infty$ is the same as the limit $\nu\to 0$.
(d) Draw a rough graph of C as a function of T.

33. Draw a rough graph of the function

$$y = \frac{\tan(x)}{x}$$

in the interval $-\pi/2 < x < \pi/2$. Use l'Hôpital's rule to evaluate the function at $x = 0$.

34. Find the relative maxima and minima of the function $f(x) = x^3 + 3x^2 - 2x$ for all real values of x.

35. The van der Waals equation of state is

$$\left(P+\frac{n^2 a}{V^2}\right)(V-nb) = n\mathrm{RT}.$$

When the temperature of a given gas is equal to its critical temperature, the gas has a state at which the pressure as a function of V at constant T and n exhibits an inflection point at which $dP/dV = 0$ and $d^2P/dV^2 = 0$. This inflection point corresponds to the critical point of the gas. Write P as a function

of T, V, and n and write expressions for $\mathrm{d}P/\mathrm{d}V$ and $\mathrm{d}^2P/\mathrm{d}V^2$, treating T and n as constants. Set these two expressions equal to zero and solve the simultaneous equations to find an expression for the pressure at the critical point.

36. Carry out Newton's method to find the smallest positive root of the equation

$$5.000x - e^x = 0.$$

Do the calculation by hand and verify your result by use of Excel.

37. Solve the following equations by hand, using the Newton–Raphson method. Verify your results using Excel or Mathematica:

(a) $e^{-x} - 0.5x = 0.$
(b) $\sin(x)/x - 0.75 = 0.$

Chapter 7

Integral Calculus

Principal Facts and Ideas

- The antiderivative $F(x)$ of $f(x)$ is the function such that $\mathrm{d}F/\mathrm{d}x = f(x)$.
- An indefinite integral is the same thing as the antiderivative function.
- A definite integral is the limit of a sum of terms $f(x)\Delta x$ in the limit that Δx approaches zero, where $f(x)$ is the integrand function.
- A definite integral equals the indefinite integral evaluated at the upper limit minus the indefinite integral evaluated at the lower limit:

$$\int_a^b f(x)\mathrm{d}x = F(b) - F(a).$$

- An improper integral has at least one infinite limit or has an integrand function that is infinite somewhere in the interval of integration. If an improper integral has a finite value, it is said to converge. Otherwise it is said to diverge.
- Mathematical methods can sometimes be used to transform an integral into a more easily computed form.
- Numerical methods exist to compute accurate approximations to integrals that cannot be performed mathematically.

Objectives

After studying this chapter, you should be able to:

- obtain the indefinite integral of an integrand function using a table;
- obtain a definite integral using the indefinite integral;
- understand the relationship of a definite integral to an area in a graph of the integrand function;
- obtain an approximate value for a definite integral using numerical analysis;
- manipulate integrals into tractable forms by use of partial integration, the method of substitution, and the method of partial fractions.

7.1 THE ANTIDERIVATIVE OF A FUNCTION

In Chapter 6, we discussed the derivative of a function. In this chapter we consider the reverse problem, finding a function that possesses a specific derivative. We call such a function an *antiderivative*. As an example, we consider the position, velocity, and acceleration of a particle.

7.1.1 Position, Velocity, and Acceleration

If a particle moves only in the vertical direction, we can express its position as a function of time:

$$z = z(t). \tag{7.1}$$

The *velocity* is the derivative of the position with respect to time. For motion in the z direction

$$v_z = v_z(t) = \frac{\mathrm{d}z}{\mathrm{d}t}. \tag{7.2}$$

The *acceleration* is the derivative of the velocity with respect to time, or the second derivative of the position.

$$a_z = \frac{\mathrm{d}v_z}{\mathrm{d}t} = \frac{\mathrm{d}^2 z}{\mathrm{d}t^2}. \tag{7.3}$$

If the particle moves in three dimensions, the position, velocity, and acceleration are vectors. The x and y components are defined in the same way as the z components.

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00007-0

If the acceleration is given as a function of time, we can construct the velocity and the position if enough initial conditions are given:

Example 7.1. If there is no other force acting on it, a particle of mass m near the surface of the earth has a downward gravitational acceleration equal to $a_z = -g$, where g is called the *acceleration due to gravity* and is equal to 9.80 m s^{-2}.[1]

(a) The particle has no other force acting on it so that its acceleration is $a_z = -g$. Find expressions for its velocity and position.

Since $-gt$ is a function that possesses $-g$ as its derivative, one possibility for the velocity is

$$v_z(t) = -gt.$$

The most general possibility is

$$v_z(t) = v_0 - gt,$$

where v_0 is a constant. This equation represents a family of functions, one function for each value of v_0. To find the position, we seek a function that has $v_0 - gt$ as its derivative. We know that

$$\frac{\mathrm{d}}{\mathrm{d}t}(at^2) = 2at \quad \text{and} \quad \frac{\mathrm{d}}{\mathrm{d}t}(at) = a,$$

so that

$$z = z(t) = z_0 + v_0 t - \frac{gt^2}{2},$$

where z_0 is again a constant. The values of the constants z_0 and v_0 must be given to determine completely the motion of the particle.

(b) Find the expression for the velocity and the position of the particle, given that the velocity at $t = 0.000$ s is 10.00 m s^{-1} and that the position at this time is $z = 0.000$ m.

$$v_z(t) = v_z(0) - gt = 10.00 \text{ m s}^{-1} - (9.80 \text{ m s}^{-2})t.$$

The position is now given by

$$z = z(t) = z_0 + (10.00 \text{ m s}^{-1})t - \frac{(9.80 \text{ m s}^{-2})t^2}{2}.$$

In order to make the position at time $t = 0.00$ s, we must let z_0 equal to zero. The position is given by

$$(10.00 \text{ m s}^{-1})t - \frac{(9.80 \text{ m s}^{-2})t^2}{2}.$$

This formula represents a parabola with a maximum height.

Exercise 7.1. Find the maximum height for the particle in the preceding example.

Example 7.2. Find the antiderivative of

$$f(x) = a \sin(bx),$$

where a and b are constants.

From Table 6.1 the antiderivative function is

$$F(x) = -\frac{a}{b}\cos(bx) + c,$$

where c is an arbitrary constant. You can differentiate to verify that

$$\frac{\mathrm{d}F}{\mathrm{d}x} = f(x).$$

Exercise 7.2. Find the function whose derivative is $-(10.00)e^{-5.00x}$ and whose value at $x = 0.00$ is 10.00.

7.2 THE PROCESS OF INTEGRATION

Say that we have a function $f = f(x)$, and we want to find its antiderivative function, $F(x)$:

$$\frac{\mathrm{d}F}{\mathrm{d}x} = f(x). \tag{7.4}$$

In Chapter 6 we wrote an approximate formula for an increment in a function:

$$\Delta F = F(x_1) - F(x_0) \approx \left(\frac{\mathrm{d}F}{\mathrm{d}x}\right)_{x=x_0} \Delta x, \tag{7.5}$$

where $\Delta x = x_1 - x_0$. This approximation becomes more nearly exact if Δx is small. If we want the value of F at some point x' that is not close to $x = x_0$, we can get a better approximation by using this equation several times. Say that we want the value of F at $x = x'$. We divide the interval between x_0 and x' into n equal subintervals. We now write

$$F(x') - F(x_0) \approx \left(\frac{\mathrm{d}F}{\mathrm{d}x}\right)_{x=x_0} \Delta x + \left(\frac{\mathrm{d}F}{\mathrm{d}x}\right)_{x=x_1} \Delta x + \cdots + \left(\frac{\mathrm{d}F}{\mathrm{d}x}\right)_{x=x_{n-1}} \Delta x, \tag{7.6}$$

where Δx is the length of each subinterval:

$$\Delta x = x_1 - x_0 = x_2 - x_1 = x_3 - x_2 = \cdots = x' - x_{n-1}. \tag{7.7}$$

[1] The acceleration due to gravity depends slightly on latitude. This value applies at 38° latitude, roughly the latitude of Washington, D.C. and Seoul, South Korea.

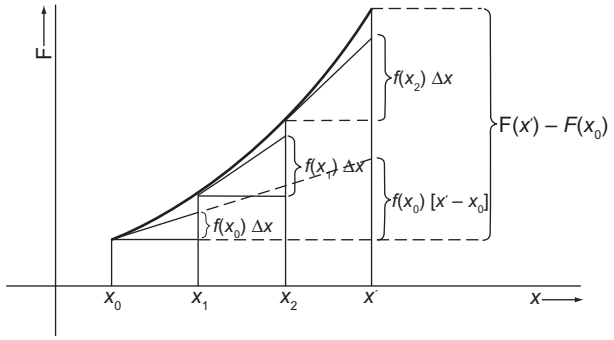


FIGURE 7.1 Figure to illustrate the summation process.

This construction is depicted in Figure 7.1, with n equal to 3. If we make n large enough, we can make the approximation nearly exact. Let us now rewrite Eq. (7.6), using the symbol $f = f(x)$ instead of $\mathrm{d}F/\mathrm{d}x$,

$$F(x') - F(x_0) \approx f(x_0)\Delta x + f(x_1)\Delta x + \cdots + f(x_{n-1})\Delta x \tag{7.8}$$

$$\approx \sum_{k=0}^{n-1} f(x_k)\Delta x. \tag{7.9}$$

We have introduced the standard notation for a sum , a capital Greek sigma (Σ). The initial value of the *summation index* k is given under the capital sigma and its final value is given above it. Unless otherwise stated, k is incremented by unity for each term. There are n terms indicated in this sum. We recognize that

$$x_k = x_0 + k\Delta x \tag{7.10}$$

and use this to write

$$F(x') - F(x_0) \approx \sum_{k=0}^{n-1} f(x_0 + k\Delta x)\Delta x. \tag{7.11}$$

We now make Eq. (7.11) into an exact equation by taking the limit as n becomes larger and larger without bound, meanwhile making Δx smaller and smaller so that $n\Delta x$ remains equal to $x' - x_0$.

$$F(x') - F(x_0) = \lim_{\substack{\Delta x \to 0, n \to \infty, \\ n\Delta x = x' - x_0}} \times \left[\sum_{k=0}^{n-1} f(x_0 + k\Delta x)\Delta x \right]. \tag{7.12}$$

The right-hand side of Eq. (7.12) is a *definite integral*. The function $f(x)$ is called the *integrand function*. The notation in this equation is cumbersome, so another symbol is used:

$$F(x') - F(x_0) = \lim_{\substack{\Delta x \to 0, n \to \infty, \\ n\Delta x = x' - x_0}} \left[\sum_{k=0}^{n-1} f(x_0 + k\Delta x)\Delta x \right] = \int_{x_0}^{x'} f(x)\mathrm{d}x. \tag{7.13}$$

The *integral sign* $\int$ on the right-hand side of Eq. (7.13) is a stretched-out letter "S," standing for a sum. However, an integral is not just a sum. It is the limit that a sum approaches as the number of terms in the sum becomes infinite in a specific way. The value x_0 is called the *lower limit of integration*, and the value x' is called the *upper limit of integration*. We now have

$$\boxed{F(x)|_{x_0}^{x'} = F(x') - F(x_0) = \int_{x_0}^{x'} f(x)\mathrm{d}x}. \tag{7.14}$$

The left-hand side of this equation contains a conventional symbol for a definite integral: a vertical line segment following the antiderivative function with the lower limit written at the bottom and the upper limit written at the top. Equation (7.14) is often called the *fundamental theorem of integral calculus*. The antiderivative function F is called the *indefinite integral* of the integrand function f.

If we can identify the antiderivative functions, we can evaluate a definite integral.

Example 7.3. Evaluate the definite integral

$$\int_0^{\pi} \sin(x)\mathrm{d}x.$$

From our table of derivatives we find the antiderivative function:

$$-\cos(x) + C = F(x).$$

Since the derivative of any constant vanishes, we have added a *constant of integration*, denoted by C. Denote the definite integral by the letter I:

$$\begin{aligned} I &= F(x)|_0^{\pi} = F(\pi) - F(0) \\ &= -\cos(\pi) + C - [-\cos(0) + C] \\ &= -\cos(\pi) + \cos(0) = -(-1) + 1 = 2. \end{aligned}$$

The constant C cancels. From now, we will omit constants of integration in definite integrals, since they always cancel.

A definite integral is not a function of its integration variable, called x in this case. Its value depends only on what values are chosen for the limits and on what function occurs under the integral sign. It is called a *functional*, or a function of a function, because its value is determined by the integrand function that is chosen.

Exercise 7.3. Evaluate the definite integral

$$\int_0^1 e^x\,\mathrm{d}x.$$

7.2.1 The Definite Integral as an Area

A definite integral is equal in value to an area between the x axis and the curve representing the integrand function. We return to Eq. (7.9),

$$F(x') - F(x_0) \approx \sum_{k=0}^{n-1} f(x_k)\Delta x. \tag{7.15}$$

This equation gives an approximation to a definite integral. Figure 7.2 shows the situation with $n = 3$.

The curve in the figure represents the integrand function $f(x)$. Each term in the sum in Eq. (7.15) is equal to the area of a rectangle with height $f(x_k)$ and width Δx, so that the sum is equal to the shaded area under the bar graph in the figure. As the limit of Eq. (7.12) is taken, the number of bars between $x = x_0$ and $x = x'$ becomes larger and larger, while the width Δx becomes smaller and smaller. The roughly triangular areas between the bar graph and the curve become smaller and smaller, and although there are more and more of them their total area shrinks to zero as the limit is taken. The integral thus becomes equal to the area bounded by the x axis, the curve of the integrand function, and the vertical lines at the limits $x = x_0$ and $x = x'$. If $x_0 < x'$, the increment Δx is positive, so that if the integrand function is negative in some region, we must take the area in that region as negative.

Example 7.4. Find the area bounded by the x-axis and the curve representing

$$f(x) = \sin(x).$$

(a) between $x = 0$ and $x = \pi$,

$$\begin{aligned}\text{Area} &= \int_0^{\pi} \sin(x)\mathrm{d}x = -\cos(\pi) - [-\cos(0)] \\ &= -\cos(\pi) - [-\cos(0)] \\ &= 2,\end{aligned}$$

(b) between $x = 0$ and $x = 2\pi$,

$$\begin{aligned}\text{Area} &= \int_0^{2\pi} \sin(x)\mathrm{d}x = -\cos(2\pi) - [-\cos(0)] \\ &= -\cos(2\pi) - [-\cos(0)] \\ &= -(1) - [-(-1)] = 0.\end{aligned}$$

The graph of the function in this example is shown in Figure 7.3.

Exercise 7.4. Find the area bounded by the curve representing $y = x^3$, the positive x axis, and the line $x = 3$.

Before the advent of programmable computers and electronic calculators, numerical approximations to integrals were sometimes made by drawing an accurate graph of the integrand function and directly measuring the appropriate area in the graph. There were three practical ways to do this. One way was by counting squares on the graph paper that was used. Another way was by cutting out the area to be determined and weighing this piece of graph paper and weighing another piece of known area from the same sheet. A third was by using a mechanical device called a *planimeter*, which registers an area on a dial after a stylus is moved around the boundary of the area. Such procedures are now seldom used, since numerical approximations can be done quickly and easily with computer software.

Exercise 7.5. Find the approximate value of the integral

$$\int_0^1 e^{-x^2}\mathrm{d}x,$$

by making a graph of the integrand function and measuring an area.

7.2.2 Facts about Integrals

The following facts about definite integrals are frequently useful:

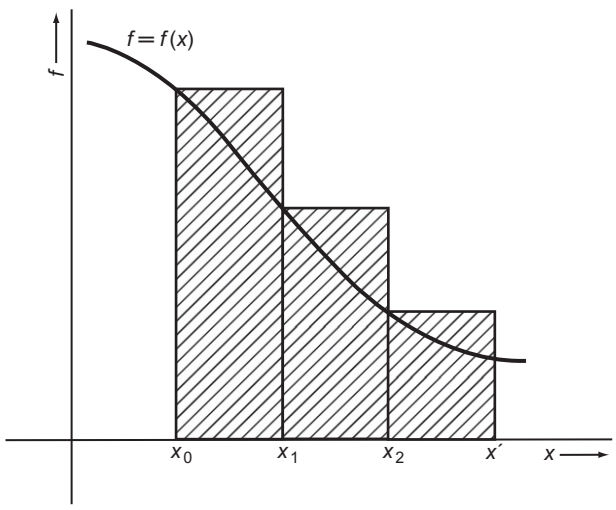


FIGURE 7.2 The area under a bar graph and the area under a curve.

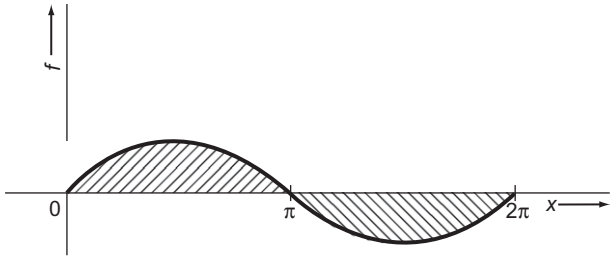


FIGURE 7.3 A graph of $f = \sin(x)$ for Example 7.6.

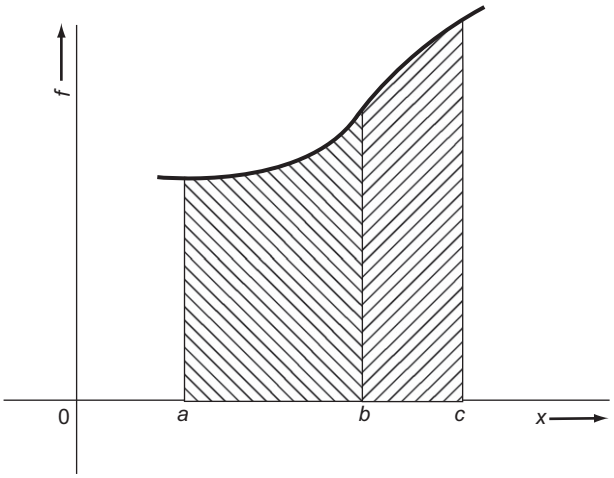


FIGURE 7.4 Figure to illustrate Eq. (4.24).

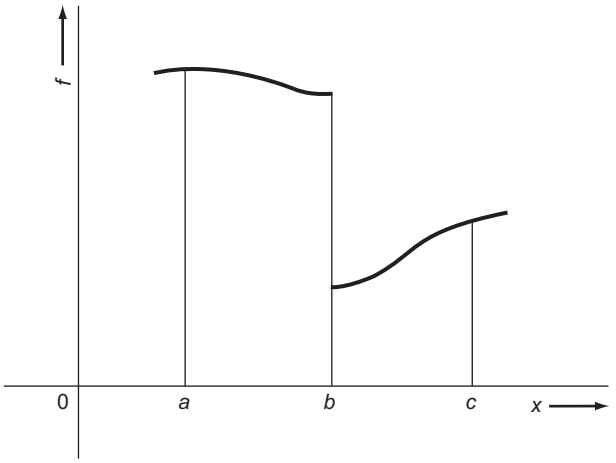


FIGURE 7.5 An integrand function that is discontinuous at $x = b$.

- A definite integral over the interval (a,c) is the sum of the definite integrals over the intervals (a,b) and (b,c):

$$\int_a^c f(x)\mathrm{d}x = \int_a^b f(x)\mathrm{d}x + \int_b^c f(x)\mathrm{d}x. \quad (7.16)$$

  This fact is illustrated in Figure 7.4. The integral on the left-hand side of Eq. (7.16) is equal to the entire area shown, and each of the two terms on the right-hand side is equal to one of the two differently shaded areas that combine to make the entire area.
- If the limits of integration are interchanged, the resulting integral is the negative of the original integral. In Eq. (7.14), we assumed that $x_0 < x'$, so that Δx would be positive. If the lower limit x_0 is larger than the upper limit of integration x', Δx is negative, reversing the sign of the area in the graph. Therefore,

$$\int_a^b f(x)\mathrm{d}x = -\int_b^a f(x)\mathrm{d}x. \quad (7.17)$$

  Use of this fact makes Eq. (7.16) usable for any real values of a, b, and c. It is not necessary for b to lie between a and c.
- The presence of a finite step discontinuity in an integrand function does not prevent us from carrying out the process of integration. Figure 7.5 illustrates the situation. If the discontinuity is at $x = b$, we simply apply Eq. (7.16) and find that the integral is given by the integral up to $x = b$ plus the integral from $x = b$ to the end of the interval.
- If an integrand function consists of a constant times some other function, the constant can be factored out of the integral:

$$\int_a^b cf(x)\mathrm{d}x = c\int_a^b f(x)\mathrm{d}x. \quad (7.18)$$

- The integral of an odd function from $-c$ to c vanishes, where c is a constant. In this case, the area above the axis exactly cancels the area below the axis, so that

$$\int_{-c}^c f(x)\mathrm{d}x = 0 \quad (f(x) \text{ odd}). \quad (7.19)$$

  An *odd function* is one that obeys the relation

$$f(-x) = -f(x). \quad (7.20)$$

  The sine function and the tangent function are examples of odd functions.

Exercise 7.6. Draw a rough graph of $f(x) = x\,e^{-x^2}$ and satisfy yourself that this is an odd function. Identify the area in this graph that is equal to the following integral and satisfy yourself that the integral vanishes:

$$\int_{-2}^2 x\,e^{-x^2}\mathrm{d}x = 0.$$

- The integral of an even function from $-c$ to c is twice the integral from 0 to c.

$$\int_{-c}^c f(x)\mathrm{d}x = 2\int_0^c f(x)\mathrm{d}x \ (f(x) \text{ even}). \quad (7.21)$$

  An *even function* is one that obeys the relation

$$f(-x) = f(x). \quad (7.22)$$

  The cosine function is an example of an even function.

Exercise 7.7. Draw a rough graph of $f(x) = e^{-x^2}$. Satisfy yourself that this is an even function. Identify the area in the graph that is equal to the definite integral

$$I_1 = \int_{-3}^3 e^{-x^2}\mathrm{d}x$$

and satisfy yourself that this integral is equal to twice the integral

$$I_2 = \int_0^3 e^{-x^2} \mathrm{d}x = 2I_1.$$

If you have an integrand that is a product of several factors, you can use the following facts about odd and even functions:

- The product of two even functions is an even function.
- The product of two odd functions is an even function.
- The product of an odd function and an even function is an odd function.

The rules about odd and even functions are valid if the function is either even or odd about the center of the integration interval, even if the center of the interval is not at the origin.

The quantum-mechanical wave functions of a particle in a box such that $0 \prec x \prec a$ are either even or odd functions about the center of the interval. For example, if the box extends from $x = 0$ to $x = a$, the two lowest-energy wave functions are

$$\psi_1 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right), \tag{7.23}$$

$$\psi_2 = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi x}{a}\right). \tag{7.24}$$

Exercise 7.8.

(a) By drawing rough graphs, satisfy yourself that ψ_1 is even about the center of the box. That is, $\psi_1(x) = \psi_1(a - x)$. Satisfy yourself that ψ_2 is odd about the center of box.

(b) Draw a rough graph of the product $\psi_1\psi_2$ and satisfy yourself that the integral of this product from $x = 0$ to $x = a$ vanishes.

7.2.3 Derivatives of Definite Integrals

If the upper limit of a definite integral is considered to be a variable, the derivative of the integral is given by

$$\frac{\mathrm{d}}{\mathrm{d}y}\left[\int_a^y f(x)\mathrm{d}x\right] = f(y), \tag{7.25}$$

where a is considered to be a constant. If the lower limit is considered to be a variable,

$$\frac{\mathrm{d}}{\mathrm{d}z}\left[\int_z^b f(x)\mathrm{d}x\right] = -f(z), \tag{7.26}$$

where b is considered to be a constant. If a and b are functions of some variable z (not the variable of integration, x), then

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}z}\left[\int_a^b f(x)\mathrm{d}x\right] = f(b)\frac{\mathrm{d}b}{\mathrm{d}z} - f(a)\frac{\mathrm{d}a}{\mathrm{d}z}}. \tag{7.27}$$

These equations follow from Eq. (7.14). Equation (7.27) also comes from the chain rule.

Example 7.5. Evaluate the following:

$$\frac{\mathrm{d}}{\mathrm{d}y}\int_0^y e^x \,\mathrm{d}x,$$

for $y = 2.00$.

$$\frac{\mathrm{d}}{\mathrm{d}y}\int_0^y e^x \,\mathrm{d}x = e^y = e^{2.00} = 7.389.$$

7.3 TABLES OF INDEFINITE INTEGRALS

Let us consider the upper limit x' in Eq. (7.14) to be variable and the lower limit to be fixed and equal to a:

$$\int_a^{x'} f(x)\mathrm{d}x = F(x') - F(a) = F(x') + C. \tag{7.28}$$

Since a is a constant, $-F(a)$ equals a constant, which we denote by C. It is the same as the *constant of integration*. The value of C is arbitrary if a is arbitrary. We omit mention of a and write

$$\int^{x'} f(x)\mathrm{d}x = F(x') + C. \tag{7.29}$$

This integral is called an *indefinite integral*, since the lower limit is unspecified and the upper limit is variable. The function $F(x)$ is the same as the antiderivative function. Although we could use a table of derivatives to find antiderivatives, it is more convenient to have tables of antiderivative functions (indefinite integrals) arranged with indefinite integrals of similar integrands placed together. Large tables of indefinite integrals have been compiled.[2] Appendix E is a brief version of such a table. In such tables, the notation of Eq. (7.29) is not maintained. The upper limit and the constant of integration are omitted, and the same symbol is usually used for the variable of integration and for the argument of the indefinite integral F. The entries are written in the form

$$\int f(x)\mathrm{d}x = F(x). \tag{7.30}$$

You should remember that an arbitrary constant C can be added to the right-hand side of Eq. (7.30).

Example 7.6. Using Appendix E, find the indefinite integrals:

[2] A very nice small volume that contains tables of integrals and other mathematical data is Herbert Bristol Dwight, *Tables of Integrals and Other Mathematical Data*, Fourth Edition, Macmillan, New York, 1957. This book is out of print, but is apparently still available through Amazon.com.

(a) $\int \dfrac{\mathrm{d}x}{a^2+x^2}$

$$\int^{x'} \frac{\mathrm{d}x}{a^2+x^2} = \frac{1}{a}\arctan\left(\frac{x'}{a}\right) + C.$$

(b) $\int x\sin^2(x)\mathrm{d}x$

$$\int^{x'} x\sin^2(x)\mathrm{d}x = \frac{x'^2}{4} - \frac{x'\sin(2x')}{4} - \frac{\cos(2x')}{8} + C. \quad (7.31)$$

(c) $\int x\,e^{ax}\,\mathrm{d}x$

$$\int^{x'} x\,e^{ax}\,\mathrm{d}x = \frac{e^{ax'}}{a^2}(ax'-1) + C.$$

Since the indefinite integral is the antiderivative function, it is used to find a definite integral in the same way as in Section 7.2. If x_1 and x_2 are the limits of the definite integral,

$$\int_{x_1}^{x_2} f(x)\mathrm{d}x = F(x_2) - F(x_1) = F(x)|_{x_1}^{x_2}. \quad (7.32)$$

Equation (7.32) is the same as Eq. (7.14).

Example 7.7. From Appendix E, find the definite integral

$$\int_0^{\pi/2} \sin(x)\cos(x)\mathrm{d}x = \frac{\sin^2(x)}{2}\bigg|_0^{\pi/2} = \frac{1}{2}\left[\sin^2\left(\frac{\pi}{2}\right) - \sin^2(0)\right] = \frac{1}{2}(1-0) = \frac{1}{2}.$$

Exercise 7.9. Using a table of indefinite integrals, find the definite integral.

$$\int_{0.000}^{3.000} \cosh(2x)\mathrm{d}x.$$

In addition to tables of indefinite integrals, there are tables of definite integrals. Some published tables are listed at the end of the book, and Appendix F is a short table of definite integrals. Some of the entries in these tables are integrals that could be worked out by using a table of indefinite integrals, but others are integrals that cannot be obtained as indefinite integrals, but by some particular method such entries can be worked out for one set of limits. An example of such an integral is worked out in Appendix G. Tables of definite integrals usually include only sets of limits such as $(0,1),(0,\pi),(0,\frac{\pi}{2})$, and $(0,\infty)$. The last set of limits corresponds to an improper integral, which is discussed in the next section.

7.4 IMPROPER INTEGRALS

If either limit of a definite integral is infinite or if the integrand is infinite anywhere inside the range of integration, the integral is said to be an *improper integral*. For example, if the upper integration limit is infinite

$$I = \int_0^\infty f(x)\mathrm{d}x, \quad (7.33)$$

we define

$$\int_0^\infty f(x)\mathrm{d}x = \lim_{b\to\infty}\int_0^b f(x)\mathrm{d}x. \quad (7.34)$$

In this mathematical limit, the upper limit of integration b becomes larger and larger without bound. Notice that the word "limit" has several definitions, and two of them unfortunately occur here in the same sentence.

If the integral approaches more and more closely to a finite value as the upper limit is made larger and larger, we say that the limit exists and that the improper integral is said to *converge* to the value that is approached. In one case, the magnitude of the integral can become larger and larger without bound as the limit of integration is made larger and larger. In other cases, the integral oscillates repeatedly in value as the limit of integration is made larger and larger. An example of the second case is

$$\int_0^\infty \sin(x)\mathrm{d}x = \lim_{b\to\infty}\int_0^b \sin(x)\mathrm{d}x. \quad (7.35)$$

As the upper limit b is made larger and larger, this integral oscillates repeatedly in value between 0 and 2, as you can see from a graph of the integrand function. We say in both of these cases that the integral *diverges*.

In addition to the type of improper integral shown in Eq. (7.33), some improper integrals have a lower limit of integration that is made to approach $-\infty$ while the upper limit is finite. Other improper integrals have both a lower limit that is made to approach $-\infty$ and an upper limit is made to approach $+\infty$. Just as in the case of Eq. (7.34), if the integral approaches a finite value more and more closely as the limit or limits approach infinite magnitude, the improper integral is said to converge to that value.

Another kind of improper integral has an integrand function that becomes infinite somewhere in the interval of integration. For example,

$$I = \int_0^1 \frac{1}{x^2}\mathrm{d}x, \quad (7.36)$$

is an improper integral because the integrand function becomes infinite at $x = 0$. This improper integral is defined by

$$\int_0^1 \frac{1}{x^2}\mathrm{d}x = \lim_{a\to 0^+}\int_a^1 \frac{1}{x^2}\mathrm{d}x. \quad (7.37)$$

Just as in the other cases, if the integral grows larger and larger in magnitude as the limit is taken, we say that it diverges. If the integral approaches more and more closely to a specific finite value, we say that the improper integral converges to that value . The situation is similar if the point at which the integrand becomes infinite is at the upper limit of integration. If it is within the interval of integration, break the interval into two subintervals so that the point at which the integrand function diverges is at the lower limit of one subinterval and at the upper end of the other subinterval.

The two principal questions that we needto ask about an improper integral are as follows:

1. Does it converge?
2. If it converges, what is its value?

Example 7.8. Determine whether the following improper integral converges, and if so, find its value:

$$\int_0^\infty e^{-x}\,\mathrm{d}x.$$

$$\int_0^\infty e^{-x}\,\mathrm{d}x = \lim_{b\to\infty}\int_0^b e^{-x}\,\mathrm{d}x = \lim_{b\to\infty}\left[-e^{-x}\right]\Big|_0^b$$
$$= \lim_{b\to\infty}\left[-(e^{-b}-1)\right] = 0+1 = 1.$$

The integral converges to the value 1.

Exercise 7.10. Determine whether each of the following improper integrals converges, and if so, determine its value:

(a) $\int_0^1 \left(\frac{1}{x}\right)\mathrm{d}x.$
(b) $\int_0^\infty \left(\frac{1}{1+x}\right)\mathrm{d}x.$

7.5 TECHNIQUES OF INTEGRATION

In this section, we discuss three methods that can be used to evaluate an integral that is not exactly like any integral you can find in a table.

7.5.1 The Method of Substitution

In the method of substitution a *change of variables* is performed. The integrand function is expressed in terms of the new independent variable, which then becomes the variable of integration. The limits of integration must be expressed in terms of the new variable.

Example 7.9. Evaluate the integral

$$\int_0^\infty xe^{-x^2}\mathrm{d}x,$$

without using a table of integrals.

We have x^2 in the exponent, which suggests using $y = x^2$ as a new variable. If $y = x^2$ then $\mathrm{d}y = 2x\,\mathrm{d}x$, or $x\,\mathrm{d}x = \frac{1}{2}\mathrm{d}y$,

$$\int_0^\infty x\,e^{-x^2}\,\mathrm{d}x = \frac{1}{2}\int_{x=0}^{x=\infty} e^{-y}\,\mathrm{d}y = \frac{1}{2}\int_0^\infty e^{-y}\,\mathrm{d}y,$$
$$= -\frac{1}{2}e^{-y}\Big|_0^\infty = -\frac{1}{2}(0-1) = \frac{1}{2}.$$

We chose a new variable that looked as though it would give a simpler integrand function. We expressed the integrand function in terms of this variable, y. Next, we expressed $\mathrm{d}x$ in terms of $\mathrm{d}y$. Next, we expressed the limits of integration in terms of the new variable. That is, we made new the limits equal to the values of the new variable that correspond to the values of the old variable at the limits.

Example 7.10. Evaluate the integral

$$\int_0^{1/2}\frac{\mathrm{d}x}{2-2x},$$

without using a table of integrals.

We let $y = 2-2x$. With this, $\mathrm{d}y = -2\,\mathrm{d}x$, or $\mathrm{d}x = -\mathrm{d}y/2$. When $x = 0, y = 2$, and when $x = \frac{1}{2}, y = 1$,

$$\int_0^{1/2}\frac{1}{2-2x}\mathrm{d}x = -\frac{1}{2}\int_2^1\frac{1}{y}\mathrm{d}y = \frac{1}{2}\int_1^2\frac{1}{y}\mathrm{d}y$$
$$= \frac{1}{2}\ln(y)\Big|_1^2 = \frac{1}{2}\left[\ln(2)-\ln(1)\right]$$
$$= \frac{1}{2}\ln(2).$$

Exercise 7.11. Evaluate the integral

$$\int_0^{\pi/2} e^{\sin(\theta)}\cos(\theta)\mathrm{d}\theta,$$

without using a table of integrals.

7.5.2 Integration by Parts

This method, which is also called *partial integration*, consists of application of the formula

$$\boxed{\int u\frac{\mathrm{d}v}{\mathrm{d}x}\mathrm{d}x = uv - \int v\frac{\mathrm{d}u}{\mathrm{d}x}\mathrm{d}x + C}, \tag{7.38}$$

where C is a constant of integration. The corresponding formula for definite integrals is

$$\boxed{\int_a^b u\frac{\mathrm{d}v}{\mathrm{d}x}\mathrm{d}x = u(x)v(x)|_a^b - \int_a^b v\frac{\mathrm{d}u}{\mathrm{d}x}\mathrm{d}x}. \tag{7.39}$$

In these formulas, u and v must be functions of x that are differentiable everywhere in the interval of integration.

We can derive Eq. (7.38) by use of Eq. (6.4), which gives the derivative of the product of two functions:

$$\frac{\mathrm{d}}{\mathrm{d}x}(uv) = u\frac{\mathrm{d}v}{\mathrm{d}x} + v\frac{\mathrm{d}u}{\mathrm{d}x}. \tag{7.40}$$

The antiderivative of either side of this equation is just $uv + C$, where C is a constant of integration. We can write the indefinite integral of this integrand

$$\int \frac{\mathrm{d}(uv)}{\mathrm{d}x}\mathrm{d}x = \int u\frac{\mathrm{d}v}{\mathrm{d}x}\mathrm{d}x + \int v\frac{\mathrm{d}u}{\mathrm{d}x}\mathrm{d}x = u(x)v(x) + C. \tag{7.41}$$

This is equivalent to Eq. (7.38).

Example 7.11. Find the indefinite integral

$$\int_0^\pi x\sin(x)\mathrm{d}x,$$

without using a table.

We could let $u(x) = x$ and $\sin(x) = \mathrm{d}v/\mathrm{d}x$ or we could let $u(x) = \sin(x)$ and $x = \mathrm{d}v/\mathrm{d}x$. We make the first choice because the antiderivative of x is $x^2/2$, which will lead to a more complicated integral than the one containing x. With this choice

$$\begin{aligned}\frac{\mathrm{d}u}{\mathrm{d}x} &= 1 \quad \text{and} \quad v = -\cos(x),\\ \int_0^\pi x\sin(x)\mathrm{d}x &= -x\cos(x)|_0^\pi + \int_0^\pi \cos(x)\mathrm{d}x\\ &= -\pi\cos(\pi) - 0 + \sin(\pi)\\ &\quad - \sin(0) = \pi.\end{aligned}$$

Exercise 7.12. Evaluate the integral

$$\int_0^\pi x^2\sin(x)\mathrm{d}x,$$

without using a table. You will have to apply partial integration twice.

The fundamental equation of partial integration, Eq. (7.38), is sometimes written with differentials instead of derivatives:

$$\boxed{\int u\,\mathrm{d}v = uv - \int v\,\mathrm{d}u + C}. \tag{7.42}$$

7.5.3 The Method of Partial Fractions

This method uses an algebraic procedure for turning a difficult integrand into a sum of two or more easier integrands. It works with an integral of the type

$$I = \int \frac{P(x)}{Q(x)}\mathrm{d}x, \tag{7.43}$$

where $P(x)$ and $Q(x)$ are polynomials. The highest power of x in P must be lower than the highest power of x in Q. Consider first the case that the polynomial $Q(x)$ can be factored into polynomials of degree 1 (of the form $ax + b$):

$$Q(x) = (a_1x + b_1)(a_2x + b_2)(a_3x + b_3)\cdots(a_nx + b_n), \tag{7.44}$$

where the a's and b's are constants. There is a theorem of algebra that says that

$$\boxed{\frac{P(x)}{Q(x)} = \frac{A_1}{a_1x + b_1} + \frac{A_2}{a_2x + b_2} + \cdots + \frac{A_n}{a_nx + b_n}}, \tag{7.45}$$

where $A_1, A_2, \ldots, A_n$ are all constants.

Equation (7.45) is applicable only if all the factors in $Q(x)$ are distinct from each other. If the factor $a_1x + b_1$ occurs m times in the denominator, the theorem implies that

$$\begin{aligned}\frac{P(x)}{(a_1x + b_1)^m} &= \frac{A_1}{a_1x + b_1} + \frac{A_2}{(a_1x + b_1)^2} + \cdots\\ &\quad + \frac{A_m}{(a_1x + b_1)^m}\\ &\quad + \text{other terms as in Eq. (7.45).}\end{aligned} \tag{7.46}$$

If other factors occur in the denominator, we must add other terms as in Eq. (7.45).

If the polynomial Q contains a factor $a_1x^2 + b_1x + c_1$, we can write

$$\begin{aligned}\frac{P(x)}{Q(x)} &= \frac{A_1x + B_1}{a_1x^2 + b_1x + c_1}\\ &\quad + \text{other terms as in Eqs. (7.45) and (7.46).}\end{aligned} \tag{7.47}$$

Example 7.12. Apply Eq. (7.45) to

$$\int \frac{6x - 30}{x^2 + 3x + 2}\mathrm{d}x.$$

The denominator can be factored into $(x + 2)(x + 1)$, so we write

$$\frac{6x - 30}{x^2 + 3x + 2} = \frac{A_1}{x + 2} + \frac{A_2}{x + 1}.$$

We need to solve for A_1 and A_2 so that this equation will be satisfied for all values of x. We multiply both sides of the equation by $(x + 2)(x - 1)$:

$$6x - 30 = A_1(x + 1) + A_2(x + 2).$$

Since this equation must be valid for all values of x, we can get a different equation for each value of x. If we let $x = 0$, we get

$$-30 = A_1 + 2A_2.$$

If we let x become very large, so that the constant terms can be neglected, we obtain

$$6x = A_1 x + A_2 x$$

or

$$6 = A_1 + A_2.$$

These equations can be solved simultaneously to obtain

$$A_1 = 42, \quad A_2 = -36.$$

Our result is

$$\int \frac{6x - 30}{x^2 + 3x + 2} \mathrm{d}x = \int \frac{42}{x + 2} \mathrm{d}x - \int \frac{36}{x + 1} \mathrm{d}x.$$

Exercise 7.13. Solve the simultaneous equations to obtain the result of the previous example.

Example 7.13. Find the indefinite integrals in the previous example.

$$\int \frac{42}{x + 2} \mathrm{d}x =: 42 \ \ln(x + 2),$$
$$\int \frac{36}{x + 1} \mathrm{d}x = 36 \ \ln(x + 1),$$
$$\int \frac{6x - 30}{x^2 + 3x + 2} \mathrm{d}x = 42 \ \ln(x + 2) - 36 \ \ln(x + 1).$$

The Apart statement in Mathematica carries out the decomposition into partial fractions automatically.

Exercise 7.14. Use Mathematica to verify the partial fractions in the above example.

The following example shows a case in the study of chemical reaction rates that requires the use of partial fractions.

Example 7.14. Consider a chemical reaction

$$a\mathrm{A} + b\mathrm{B} \longrightarrow c\mathrm{C},$$

where the capital letters are abbreviations for some chemical formulas and the lower-case letters are abbreviations for the stoichiometric coefficients that balance the equation. Assume that the rate of the reaction is given by the *rate law*

$$-\frac{1}{a}\frac{\mathrm{d[A]}}{\mathrm{d}t} = k_f[\mathrm{A}][\mathrm{B}],$$

where k_f is a function of temperature called the *rate constant* and where [A] is the molar concentration of A and [B] is the molar concentration of B. This rate law is said to be *second order overall*, *first order in A*, and *first order in B*. Carry out the integration of this rate law using the method of partial fractions.

In order to proceed, we express [A] and [B] in terms of a single variable:

$$[\mathrm{A}] = [\mathrm{A}]_0 - ax$$

and

$$[\mathrm{B}] = [\mathrm{B}]_0 - bx,$$

where the initial values of the concentrations are labeled with a subscript 0. We have

$$-\frac{1}{a}\frac{\mathrm{d[A]}}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t}.$$

In the case that the reactants are not mixed in the stoichiometric ratio, we manipulate the rate expression into the form, where we have multiplied by dt and recognized that $(\mathrm{d}x/\mathrm{d}t)\mathrm{d}t = \mathrm{d}x$,

$$\frac{1}{([\mathrm{A}]_0 - ax)([\mathrm{B}]_0 - bx)} \mathrm{d}x = k_f \, \mathrm{d}t.$$

We write

$$\frac{1}{([\mathrm{A}]_0 - ax)([\mathrm{B}]_0 - bx)} = \frac{G}{[\mathrm{A}]_0 - ax} + \frac{H}{[\mathrm{B}]_0 - bx}.$$

The constants G and H are found to be

$$G = \frac{1}{[\mathrm{B}]_0 - b[\mathrm{A}]_0/a} \quad \text{and} \quad H = \frac{1}{[\mathrm{A}]_0 - a[\mathrm{B}]_0/b}.$$

When these expressions are substituted into the rate expression, a definite integration gives

$$\frac{1}{a[\mathrm{B}]_0 - b[\mathrm{A}]_0} \ln\left(\frac{[\mathrm{B}]_t [\mathrm{A}]_0}{[\mathrm{A}]_t [\mathrm{B}]_0}\right) = k_f t.$$

Exercise 7.15. Show that the expressions for G and H are correct. Verify your result using Mathematica if it is available.

The methods presented thus far in this chapter provide an adequate set of tools for the calculation of most integrals that will be found in a physical chemistry course. In applying these methods, you can proceed as follows:

1. If the limits are 0 and ∞ or 0 and π, or something else quite simple, look for the integral in a table of definite integrals.
2. If this does not work, look in a table of indefinite integrals.
3. If you do not find the integral in a table, try the method of substitution.
4. If you still have not obtained the integral, see if the method of partial fractions is applicable and use it if you can.
5. If this did not work, manipulate the integrand into a product of two factors and try the method of partial integration.
6. If all these things have failed, or if they could not be attempted, do a numerical approximation to the integral. This is discussed in the next section.

7.5.4 Integration with Mathematica

Mathematica can carry out indefinite integrals symbolically. The input and output statements for the indefinite integral of sin(x) are

```
In[1]: = Clear[x]
         Integrate[Sin[x],x]
Out[1] = −Cos[x]
```

Mathematica appears to contain just about every indefinite integral that exists in tables. However, if you specify an integrand for which no indefinite integral exists or one that is not in Mathematica's tables, Mathematica will print out what you gave it.

Mathematica can also carry out definite integrals. Definite integrals are obtained by adding the limits to the input entry, enclosed in curly brackets. To obtain the definite integral of sin (x) from $x = 0$ to $x = \pi$, the input and output statements are

```
In[1]: =Clear[x]
         Integrate[Sin[x],{x,0,Pi}]
Out[1] =2
```

7.6 NUMERICAL INTEGRATION

There are two cases for which a numerical approximation to a definite integral must be used. In one case the integrand function does not possess an antiderivative function that you can find in a table or can work out. One integrand function for which no antiderivative functions exists is e^{-x^2} (see Appendix G). In the other case the integrand function is represented by a set of data points instead of by a formula. In either case, there are several approximation methods that we can use to obtain a definite integral.

7.6.1 The Bar-Graph Approximation

We begin with Eq. (7.13):

$$\int_a^b f(x)\mathrm{d}x = \lim_{\substack{\Delta x\to 0, n\to\infty, \\ (n\Delta x = x' - x_0)}} \sum_{k=0}^{n-1} f(a + j\Delta x)\Delta x. \tag{7.48}$$

If we do not take the limit but allow n to be some convenient finite number, the resulting equation will be approximately correct. We call this approximation the *bar-graph approximation*. The approximation to the integral is the sum of the areas of rectangular regions such that the height of each bar matches the value of the integrand function at the left edge of the "bar."

Example 7.15. Evaluate the integral

$$\int_{1.00}^{2.00} e^{-x^2}\mathrm{d}x,$$

using the bar-graph approximation. We apply an approximate version of Eq. (7.48) with $n = 10$. The result is

$$\begin{aligned}\int_1^2 e^{-x^2}\mathrm{d}x &\approx \sum_{j=0}^{9} \exp\left[-(1.00 + 0.10j)^2\right](0.1) \\ &= 0.15329.\end{aligned}$$

The correct value of the integral is

$$\int_1^2 e^{-x^2}\mathrm{d}x = 0.13525726.$$

The bar-graph approximation is in error by about 15%.

Figure 7.2 represents the bar-graph approximation. Each rectangular "bar" is called a *panel*. The bar-graph approximation can be made more nearly accurate by increasing the number of panels, but the rate of improvement can be quite slow. For example, if we take $n = 20$ and $\Delta x = 0.05$, we get 0.14413 for the bar-graph approximation to the integral in the previous example, which is still in error by about 6%. If we take $n = 100$ and $\Delta x = 0.01$, we get 0.13701, which is still in error by 1%.

7.6.2 The Trapezoidal Approximation

In the *trapezoidal approximation* the height of the bar is taken as the average of the values of the function at the two sides of the panel. This gives an area for the panel that is the same as that of a trapezoid whose upper corners match the integrand function at the sides of the panel, as shown in Figure 7.6.

$$\int_a^b f(x)\mathrm{d}x \approx \frac{f(a)\Delta x}{2} + \sum_{k=1}^{n-1} f(a + k\Delta x)\Delta x + \frac{f(b)\Delta x}{2}. \tag{7.49}$$

As expected, the trapezoidal approximation gives more nearly correct values than does the bar-graph approximation for the same number of panels. For 10 panels, the trapezoidal approximation gives a result of 0.135810 for the integral in the previous example. For 100 panels, the trapezoidal approximation result is correct to five significant digits.

Example 7.16. Using the trapezoidal approximation with five panels, calculate the value of the integral

$$\int_{10.00}^{20.00} x^2\,\mathrm{d}x.$$

Calculate the exact value of the integral for comparison.

For five panels, $\Delta x = 2.00$

$$\int_{10}^{20} 2.00x^2\,\mathrm{d}x \approx \frac{10.00^2}{2}(2.00) + (12)^2(2.00) + (14.00^2)(2.00) + (16.00)^2(2.00) + (18.00)^2(2.00) + \frac{(20.00)^2}{2}(2.00) = 2340.0.0.$$

The correct value is

$$\int_{10.00}^{20.00} x^2\,\mathrm{d}x = \frac{x^3}{3}\Big|_{10.00}^{20.00} = \frac{8000.0}{3} - \frac{1000.0}{3} = \frac{7000.0}{3} = 2333.3.$$

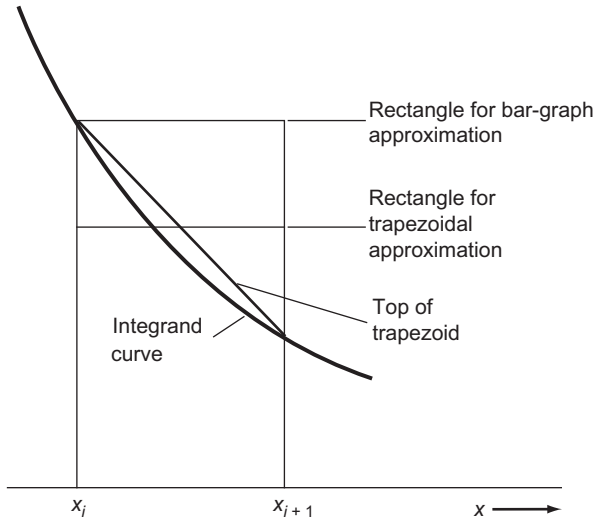


FIGURE 7.6 Figure to illustrate the trapezoidal approximation (enlarged view of one panel shown).

Exercise 7.16. Using the trapezoidal approximation, evaluate the following integral, using five panels.

$$\int_{1.00}^{2.00} \cosh(x)\mathrm{d}x.$$

7.6.3 Simpson's Rule

In the bar-graph approximation, we used only one value of the integrand for each panel. In the trapezoidal approximation, we used two values for each panel, corresponding to a line segment fitting the integrand curve at the edges of the panel. If three points in a plane are given, there is one and only one parabola that can be drawn through all three. In *Simpson's rule*, we take the panels two at a time, construct a parabola through the three points, find the area under the parabola, and sum these areas to approximate the integral. We must use an even number of panels, so that n is an even number. A parabolic curve is likely to fall closer to the integrand curve than a straight line, so we expect this to give a better approximation than the trapezoidal approximation, and it usually does.

We let $f_0 = f(a), f_1 = f(a+\Delta x), f_2 = f(a+2\Delta x)$, and so on, and use the formula for the area under a parabola to obtain as our final result

$$\int_a^b f(x)\mathrm{d}x \approx \frac{\left(f_0 + 4f_1 + 2f_2 + 4f_3 + \cdots + 4f_{n-1} + f_n\right)\Delta x}{3}. \tag{7.50}$$

Notice the pattern, with alternating coefficients of 2 and 4, except for the first and last values of the integrand.

This version of Simpson's rule is sometimes called *Simpson's one-third rule* because of the 3 in the denominator. There is another version, called *Simpson's five-eighths rule*, which corresponds to fitting third-degree polynomials to four points at a time.

Exercise 7.17. Apply Simpson's rule to the integral

$$\int_{10.00}^{20.00} x^2\,\mathrm{d}x,$$

using two panels. Since the integrand curve is a parabola, your result should be exactly correct.

There is another widely used way to obtain a numerical approximation to a definite integral, known as *Gauss quadrature*. In this method, the integrand function must be evaluated at particular unequally spaced points on the interval of integration. We will not discuss this method, but you can read about it in books on numerical analysis.

So far, we have assumed that the integrand function was known so that it could be evaluated at the required points. Most of the applications of numerical integration in physical chemistry are to integrals where the integrand function is not known exactly, but is known only approximately from experimental measurements at a few points on the interval of integration. If there are an odd number of data points that are equally spaced, we can apply Simpson's rule.

Example 7.17. In thermodynamics, it is shown that the entropy change of a system that is heated at constant pressure from temperature T_1 to temperature T_2 is given by

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_\mathrm{p}}{T}\mathrm{d}T,$$

where C_p is the constant-pressure heat capacity and T is the temperature on the Kelvin scale. Calculate ΔS for the

heating of 1.00 mol of solid zinc from 20.0 K to 100.0 K, using the following data:

(T/K)	$(C_p/\text{J K}^{-1}\text{ mol}^{-1})$	(T/K)	$(C_p/\text{J K}^{-1}\text{ mol}^{-1})$
20	1.70	70	15.43
30	4.966	80	16.87
40	8.171	90	18.11
50	11.18	100	19.15
60	13.60		

We create the following table of values.

(T/K)	$((C_p/T)/$ $\text{J K}^{-2}\text{ mol}^{-1})$	(T/K)	$((C_p/T)/$ $\text{J K}^{-2}\text{ mol}^{-1})$
20	0.0850	70	0.2204
30	0.1655	80	0.2109
40	0.2043	90	0.2012
50	0.2236	100	0.1915
60	0.2267		

$$\begin{aligned}\Delta S &= S(100.0\text{K}) - S(20.0\text{K}) = \int_{2o.0\text{K}}^{100.0\text{K}} \frac{C_p}{T}\mathrm{d}T \\ &\approx \frac{1}{3}\big[0.0850 + 4(0.1655) + 2(0.2043) \\ &\quad + 4(0.2236) + 2(0.2267) + 4(0.2204) \\ &\quad + 2(0.2109) + 4(0.2012) + 0.1915\big]\,(10.0\text{ K}) \\ &= 16.01\text{ J K}^{-1}\text{ mol}^{-1}.\end{aligned}$$

Exercise 7.18. Using Simpson's rule, calculate the integral from $x = 0.00$ to $x = 1.20$ for the following values of the integrand.

x	0.00	0.20	0.40	0.60	0.80	1.00	1.20
$f(x)$	1.000	1.041	1.174	1.433	1.896	2.718	4.220

7.6.4 Numerical Integration with Mathematica

If you give Mathematica a definite integral with an integrand that has no indefinite integral in Mathematica's tables, Mathematica will simply return your input statement. To carry out a numerical approximation to the integral and obtain a numerical value, use the *NIntegrate* statement, which has the form:

NIntegrate[integrand function, {x,lower limit,upper limit}].

Example 7.18. Use Mathematica to obtain the integral

$$\frac{2}{\sqrt{\pi}}\int_0^1 e^{-x^2}\,\mathrm{d}x \tag{7.51}$$

We type the input statements:

Clear[x]
NIntegrate[(2/Sqrt[Pi])Exp[-x^2],{x,0,1}]
and press the "Enter" key. We obtain the output
Out[1]=0.842701
which is the value of erf(1).

Exercise 7.19. Write Mathematica entries to obtain the following integrals:

(a) $\int \cos^3(x)\mathrm{d}x$.
(b) $\int_1^2 e^{5x^2}\mathrm{d}x$.

PROBLEMS

1. Find the indefinite integral without using a table:

(a) $\int x\ln(x)\mathrm{d}x$.
(b) $\int x\sin^2(x)\mathrm{d}x$.

2. Find the indefinite integral without using a table: $\int \frac{1}{x(x-a)}\mathrm{d}x$.

3. Evaluate the definite integrals, using a table of indefinite integrals

(a) $\int_{1.000}^{2.000} \frac{\ln(3x)}{x}\mathrm{d}x$.
(b) $\int_{0.000}^{5.000} 4^x\mathrm{d}x$.

4. Evaluate the definite integral: $\int_0^{2\pi}\sin(x)\mathrm{d}x$.

5. Evaluate the definite integral: $\int_2^4 \frac{1}{x\ln(x)}\mathrm{d}x$.

6. Evaluate the definite integral: $\int_0^{\pi/2}\sin(x)\cos(x)\mathrm{d}x$.

7. Evaluate the definite integral: $\int_2^{10} x\ln(x)\mathrm{d}x$.

8. Evaluate the definite integral: $\int_0^{\pi/2}\sin(x)\cos^2(x)\mathrm{d}x$.

9. Evaluate the definite integral: $\int_0^{\pi/2} x\sin(x^2)\mathrm{d}x$.

10. Evaluate the definite integral: $\int_0^{\pi/2} x\sin(x^2)\cos(x^2)\mathrm{d}x$.

11. Find the following area by computing the values of a definite integral: The area bounded by the straight line $y = 2x + 3$, the x axis, the line $x = 1$, and the line $x = 4$.

12. Find the following area by computing the values of a definite integral. The area bounded by the parabola $y = 4 - x^2$ and the x axis. You will have to find the limits of integration.

13. Determine whether each of the following improper integrals converges, and if so, determine its value:

(a) $\int_0^\infty \frac{1}{x^3}\mathrm{d}x$.
(b) $\int_{-\infty}^0 e^x\,\mathrm{d}x$.

14. Determine whether the following improper integrals converge. Evaluate the convergent integrals.

(a) $\int_1^\infty \left(\frac{1}{x^2}\right)\mathrm{d}x$.
(b) $\int_1^{\pi/2} \tan(x)\mathrm{d}x$.

15. Determine whether the following improper integrals converge. Evaluate the convergent integrals

(a) $\int_0^1 \frac{1}{x\ln(x)}\mathrm{d}x$.
(b) $\int_1^\infty \left(\frac{1}{x}\right)\mathrm{d}x$.

16. Determine whether the following improper integrals converge. Evaluate the convergent integrals $\int_0^\pi \tan(x)\mathrm{d}x$.

(a) $\int_0^{\pi/2} \tan(x)\mathrm{d}x$.
(b) $\int_0^1 \left(\frac{1}{x}\right)\mathrm{d}x$.

17. Determine whether the following improper integrals converge. Evaluate the convergent integrals,

(a) $\int_0^\infty \sin(x)\mathrm{d}x$.
(b) $\int_{-\pi/2}^{\pi/2} \tan(x)\mathrm{d}x$.

18. Approximate the integral

$$\int_0^\infty e^{-x^2}\,\mathrm{d}x,$$

using Simpson's rule. You will have to take a finite upper limit, choosing a value large enough so that the error caused by using the wrong limit is negligible. The correct answer is $\sqrt{\pi}/2 = 0.886226926\cdots$.

19. Using Simpson's rule, evaluate erf (2.000):

$$\mathrm{erf}(2) = \frac{2}{\sqrt{\pi}}\int_0^2 e^{-t^2}\mathrm{d}t.$$

Compare your answer with the correct value from a more extended table than the table in Appendix G, $erf\,(2.000) = 0.995322265$.

20. Find the integral: $\int \sin\left[x(x+1)\right](2x+1)\mathrm{d}x$.

21. Find the integral: $\int x\ln(x^2)\mathrm{d}x$.

22. When a gas expands reversibly, the work that it does on its surroundings is given by the integral

$$w_{\mathrm{surr}} = \int_{V_1}^{V_2} P\,\mathrm{d}V,$$

where V_1 is the initial volume, V_2 is the final volume, and P is the pressure of the gas. Certain nonideal gases are described by the van der Waals equation of state,

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT,$$

where V is the volume, n is the amount of gas in moles, T is the temperature on the Kelvin scale, and a and b are constants. R is usually taken to be the ideal gas constant, 8.3145 J K^{-1} mol^{-1}.

(a) Obtain a formula for the work done on the surroundings if 1.000 mol of such a gas expands reversibly at constant temperature from a volume V_1 to a volume V_2.
(b) If $T = 298.15$ K, $V_1 = 1.001$l $(1.000 \times 10^{-3}$ $m^3)$, and $V_2 = 100.0$l $= 0.100$ m^3, find the value of the work done for 1.000 mol of CO_2, which has $a = 0.3640$ Pa m^6 mol^{-2} and $b = 4.267 \times 10^{-5}$ m^3 mol^{-1}. The ideal gas constant, $R = 8.3145$ J K^{-1} mol^{-1}.
(c) Calculate the work done in the process of part b if the gas is assumed to be ideal.

23. The entropy change to bring a sample from 0 K (absolute zero) to a given state is called the *absolute entropy* of the sample in that state.

$$S_m(T') = \int_0^{T'} \frac{C_{\mathrm{P},m}}{T}\mathrm{d}T,$$

where $S_m(T\prime)$ is the absolute molar entropy at temperature T', $C_{\mathrm{P},m}$ is the molar heat capacity at constant pressure, and T is the absolute temperature. Using Simpson's rule, calculate the absolute entropy of 1.000 mol of solid silver at 270 K. For the region 0–30 K, use the approximate relation

$$C_{\mathrm{p}} = aT^3,$$

where a is a constant that you can evaluate from the value of C_{p} at 30 K. For the region 30–270 K, use the following data:[3]

T/K	C_{P}/J K^{-1} mol^{-1}	T/K	C_{P}/J K^{-1} mol^{-1}
30	4.77	170	23.61
50	11.65	190	24.09
70	16.33	210	24.42
90	19.13	230	24.73
110	20.96	250	25.03
130	22.13	270	25.31
150	22.97		

[3] Meads. Forsythe, and Giaque, *J. Am. Chem. Soc*. **63**, 1902 (1941).

24. Use Simpson's rule to evaluate the following definite integral. Use Mathematica to check your results.

$$\int_0^2 e^{-3x^3}\,\mathrm{d}x.$$

25. Use Simpson's rule with at least four panels to evaluate the following definite integral. Use Mathematica to check your results.

$$\int_1^3 e^{2x^2}\,\mathrm{d}x.$$

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Chapter 8

Differential Calculus with Several Independent Variables

Principal Facts and Ideas

- Functions of several independent variables occur frequently in physical chemistry, both in thermodynamics and in quantum mechanics.
- A derivative of a function of several variables with respect to one independent variable is called a partial derivative. The other variables are treated as constants during the differentiation.
- There are some useful identities that allow manipulations of expressions containing partial derivatives.
- The differential of a function of several variables (an exact differential) has one term for each variable, consisting of a partial derivative times the differential of the independent variable. This differential form delivers the value of an infinitesimal change in the function produced by infinitesimal changes in the independent variables.
- Differential forms exist that are not the differentials of any function. Such a differential form is called an inexact differential.
- Relative maxima and minima of a function of several variables are found by solving simultaneously the equations obtained by setting all partial derivatives equal to zero.
- Constrained maxima and minima of a function of several variables can be found by the method of Lagrange multipliers.
- The gradient operator is a vector derivative operator that produces a vector when applied to a scalar function.
- The divergence operator is a vector derivative operator that produces a scalar when applied to a vector function.
- The curl operator is a vector derivative operator that produces a vector when applied to a vector function.
- The Laplacian operator is equivalent to the divergence of the gradient of a scalar function.

Objectives

After studying this chapter, you should be able to:

- write formulas for the partial derivatives and for the differential of a function if given a formula for the function and use these in applications such as the calculation of small changes in a dependent variable;
- perform a change of independent variables and obtain formulas relating different partial derivatives;
- use identities involving partial derivatives to eliminate undesirable quantities from thermodynamic formulas;
- identify an exact differential and an integrating factor;
- find constrained and unconstrained maximum and minimum values of functions of several variables;
- form the gradient, divergence, curl, and Laplacian of any relatively simple function.

8.1 FUNCTIONS OF SEVERAL INDEPENDENT VARIABLES

A function of several independent variables gives the value of a dependent variable if you specify a value for each of the independent variables. The equilibrium thermodynamic properties of a fluid (gas or liquid) system of one substance and one phase are functions of three independent variables. If we choose a set of values for the temperature, T, volume, V, and amount of the substance in moles, n, then the other thermodynamic properties, such as the pressure, P, and the

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00008-2

thermodynamic energy, U, are functions of these variables. We can write

$$P = P(T,V,n), \tag{8.1a}$$

$$U = U(T,V,n). \tag{8.2}$$

We can choose any three of the variables as independent variables so long as at least one of them is proportional to the size of the system, and the other variables are then dependent variables that depend on the three independent variables that we chose. A variable that is proportional to the size of the system is called an *extensive variable*. We could also write

$$U = U(T,P,n), \tag{8.3a}$$

$$U = U(P,V.n), \tag{8.3b}$$

and so on. A variable that is independent of the size of the system is called an *intensive variable*. If we consider only intensive variables, only two variables are independent. The molar volume, defined as V/n, is the quotient of two extensive variables, and is an intensive variable, as are the temperature and the pressure. The pressure of a fluid system of one substance depends only on the temperature and the molar volume.

We assume that the functions that represent the behavior of physical systems are *piecewise continuous* with respect to each variable. If we temporarily keep all but one of the independent variables fixed, the function behaves as a piecewise continuous function of that variable. We also assume that the functions are piecewise single-valued. That is, except at isolated points, there is one and only one value of the dependent variable for a given set of values of the independent variables.

If the temperature of a gas is fairly high and its volume is large enough, the pressure of a gas is given to a good approximation by the ideal gas equation

$$P = P(T,V_m) = \frac{RT}{V_m}, \tag{8.4}$$

where R is the ideal gas constant, equal to 8.3145 J K^{-1} mol^{-1} or 0.0820561 atm K^{-1} mol^{-1}, T is the absolute temperature, and V_m is the molar volume. Figure 8.1 shows the dependence of the pressure of a nearly ideal gas as a function of the molar volume at several fixed temperatures. With only two axes on our graph, a curve can show the dependence of P on V_m only for a fixed value of T.

Three-dimensional graphs can show the dependence of a dependent variable on two independent variables, but are much more difficult to use, since we have only two-dimensional paper and two-dimensional computer screens. Figure 8.2 is a perspective view of a three-dimensional graph representing P as a function of V_m and T. The value of P is given by the height from the horizontal plane to a surface, which plays the same role as the curve in a two-dimensional graph. It is fairly easy to read quantitative information from the two-dimensional graph in Figure 8.1, but the perspective view in Figure 8.2 is more difficult to read numbers from. If you have more than two independent

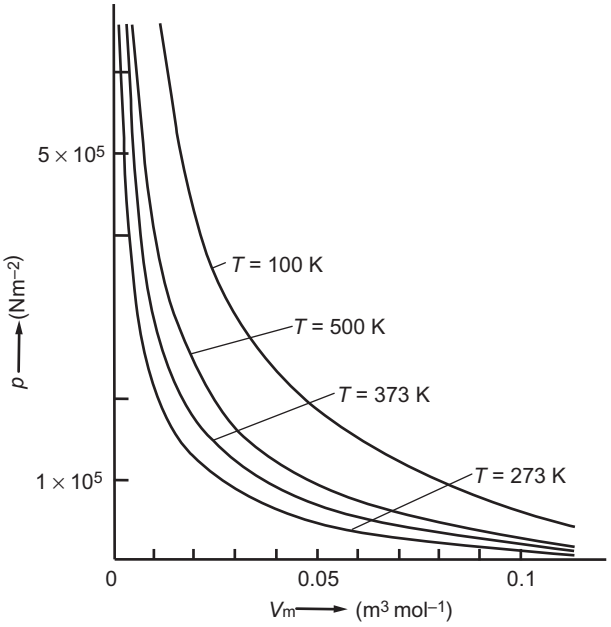

FIGURE 8.1 The pressure of a nearly ideal gas a function of V_m for several values of T.

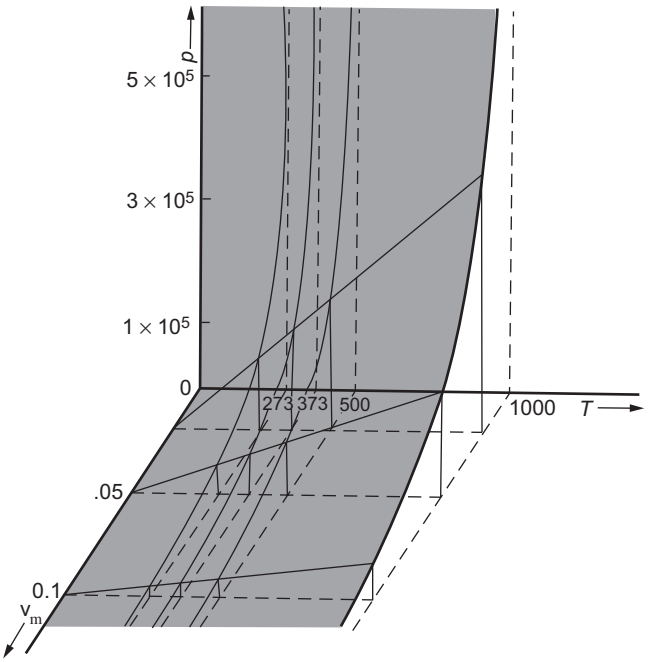

FIGURE 8.2 The pressure of a nearly ideal gas a function of V_m and T.

variables, a graph cannot be visualized. Sometimes attempts are made to show roughly how functions of three variables depend on their independent variables by drawing a perspective view of three axes, and then trying to communicate the approximate value of the dependent variable by a density of dots placed in the diagram or by contours of equal values of the dependent variable.

Tables of values are also cumbersome with two or more independent variables, since a function is now not a set of ordered pairs of numbers but a set of ordered sets of three numbers or four numbers, and so on. For two independent variables, we need a rectangular array, with values of one independent variable along the top and values of the other along one side, and values of the dependent variable in the body of the array. For a third independent variable, we would need a different sheet of paper for each value of the third variable. The most common way to represent a function of several variables is with a mathematical formula.

8.2 CHANGES IN A FUNCTION OF SEVERAL VARIABLES, PARTIAL DERIVATIVES

Consider a gas contained in a cylinder with a movable piston and a valve through which gas can be admitted or removed, and let the entire system be immersed in a constant-temperature bath so that we can control the temperature. The pressure is a function of the amount of gas n, the temperature T, and the volume V. For the present, we keep the valve closed, so that n is fixed (we say that the system is now a *closed system*). We can also keep T fixed with our constant-temperature bath. We now make an infinitesimal change $\mathrm{d}V$ in the volume of the gas, allowing the gas to come back to equilibrium after the change. If n and T are both fixed, P will behave like a function of the one variable V. The change in P is given in the same way as with a function of one variable:

$$\mathrm{d}P = \left(\frac{\mathrm{d}P}{\mathrm{d}V}\right)\mathrm{d}V \quad (n \text{ and } T \text{ fixed}), \tag{8.5}$$

where $\mathrm{d}P/\mathrm{d}V$ is the derivative of P with respect to V.

We adopt a new notation, replacing the d symbols by partial derivative symbols that are slightly distorted lowercase Greek deltas and adding subscripts to specify the variables that are fixed.

$$\mathrm{d}P = \left(\frac{\partial P}{\partial V}\right)_{n,T}\mathrm{d}V \quad (n \text{ and } T \text{ fixed}). \tag{8.6}$$

The quantity $(\partial P/\partial V)_{n,T}$ is called the *partial derivative* of P with respect to V at constant n and T. The partial derivative is obtained by the differentiation techniques of Chapter 6, treating n and T like ordinary constants. We can also keep another set of two of the three independent variables constant. There are as many partial derivatives of a given function as there are independent variables on which it depends. If the gas is adequately described by the ideal gas law, these derivatives are

$$\left(\frac{\partial P}{\partial V}\right)_{n,T} = \left(\frac{\partial}{\partial V}\left[\frac{nRT}{V}\right]\right)_{n,T} = -\frac{nRT}{V^2} \quad (n \text{ and } T \text{ fixed}), \tag{8.7}$$

$$\left(\frac{\partial P}{\partial T}\right)_{n,V} = \left(\frac{\partial}{\partial T}\left[\frac{nRT}{V}\right]\right)_{n,V} = \frac{nR}{V} \quad (n \text{ and } V \text{ fixed}), \tag{8.8}$$

$$\left(\frac{\partial P}{\partial n}\right)_{T,V} = \left(\frac{\partial}{\partial n}\left[\frac{nRT}{V}\right]\right)_{T,V} = \frac{RT}{V} \quad (T \text{ and } V \text{ fixed}). \tag{8.9}$$

Each of these partial derivatives is obtained by the usual differentiation technique, treating the other variables as constants.

8.2.1 Differentials

If we make an infinitesimal change $\mathrm{d}V$ in the volume and a change $\mathrm{d}T$ in the temperature of the gas while keeping n fixed, the change in the dependent variable P is the sum of two expressions like that in Eq. (8.6).

$$\mathrm{d}P = \left(\frac{\partial P}{\partial V}\right)_{n,T}\mathrm{d}V + \left(\frac{\partial P}{\partial T}\right)_{n,V}\mathrm{d}T \quad (n \text{ fixed}). \tag{8.10}$$

If we make the changes $\mathrm{d}V$ in V, $\mathrm{d}T$ in T, and $\mathrm{d}n$ in n, these changes affect P separately, and we can write for the total infinitesimal change in the dependent variable P,

$$\mathrm{d}P = \left(\frac{\partial P}{\partial V}\right)_{n,T}\mathrm{d}V + \left(\frac{\partial P}{\partial T}\right)_{n,V}\mathrm{d}T + \left(\frac{\partial P}{\partial n}\right)_{T,V}\mathrm{d}n. \tag{8.11}$$

The infinitesimal change $\mathrm{d}P$ given by this expression is called the *differential* of P, or sometimes the *total differential of P*. Each term gives the effect of one independent variable with the other independent variables treated as constants.

If we have a dependent variable y that depends on n independent variables, $x_1, x_2, x_3, \ldots, x_n$, its differential is

$$\boxed{\mathrm{d}y = \sum_{i=1}^{n}\left(\frac{\partial y}{\partial x_i}\right)_{x'}\mathrm{d}x_i}, \tag{8.12}$$

where the subscript x' stands for keeping all of the variables except for x_i fixed in the differentiation. This equation is

sometimes called the *fundamental equation of differential calculus*.

The expression for dP for an ideal gas is

$$\mathrm{d}P = -\frac{nRT}{V^2}\mathrm{d}V + \frac{nR}{V}\mathrm{d}T + \frac{RT}{V}\mathrm{d}n. \tag{8.13}$$

For small but finite changes, an approximate version of this equation can be written

$$\Delta P \approx -\frac{nRT}{V^2}\Delta V + \frac{nR}{V}\Delta T + \frac{RT}{V}\Delta n. \tag{8.14}$$

Example 8.1. Use Eq. (8.14) to calculate approximately the change in pressure of an ideal gas if the volume is changed from 20.000 l to 19.800 l, the temperature is changed from 298.15 K to 299.00 K, and the amount of gas in moles is changed from 1.0000 mol to 1.0015 mol. Compare the result with the correct value of the pressure change.

Using the fact that in SI units the value of the ideal gas constant, R, is equal to 8.3145 J K^{-1} mol^{-1},

$$\begin{aligned}\Delta P \approx & -\frac{(1.0000\ \text{mol})(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})}{\left(0.020000\ \text{m}^3\right)^2} \\ & \times \left(-0.200 \times 10^{-3}\ \text{m}^3\right) \\ & + \frac{(1.0000\ \text{mol})(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})}{0.020000\ \text{m}^3}\left(0.85\ \text{K}\right) \\ & + \frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})}{0.020000\ \text{m}^3}(0.0015\ \text{mol}) \\ \approx & \ 1.779 \times 10^3\ \text{N m}^{-2} = 1.779 \times 10^3\ \text{Pa},\end{aligned}$$

where we also used the fact that 1 J = 1 N m. The actual change is

$$\begin{aligned}\Delta P &= P_2 - P_1 = \frac{n_2 RT_2}{V_2} - \frac{n_1 RT_1}{V_1} \\ &= 1.797 \times 10^3\ \text{N m}^{-2} = 1.797 \times 10^3\ \text{Pa}.\end{aligned}$$

Our approximate value is in error by about 1%.

In this example the exact calculation could be made more easily than the approximation. However, in physical chemistry it is frequently the case that a representation of a function is not known, but values for the partial derivatives are available, so that approximation can be made while the exact calculation cannot. For example, there is usually no simple formula giving the thermodynamic energy as a function of its independent variables. However, we can write

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_{P,n}\mathrm{d}T + \left(\frac{\partial U}{\partial P}\right)_{T,n}\mathrm{d}P + \left(\frac{\partial U}{\partial n}\right)_{P,T}\mathrm{d}n. \tag{8.15}$$

Experimental values of these partial derivatives are frequently available, so that even if we have no representation of the function giving a value of U, we can compute an approximate value for ΔU.

$$\Delta U \approx \left(\frac{\partial U}{\partial T}\right)_{P,n}\Delta T + \left(\frac{\partial U}{\partial P}\right)_{T,n}\Delta P + \left(\frac{\partial U}{\partial n}\right)_{P,T}\Delta n. \tag{8.16}$$

Example 8.2. For a sample of 1.000 mol (0.15384 kg) of liquid carbon tetrachloride (CCl_4) at a temperature of 20 °C and a pressure of 1.000 atm, the following experimental values are available:

$$\begin{aligned}\left(\frac{\partial U}{\partial T}\right)_{P,n} &= 129.4\ J\ \text{K}^{-1}, \\ \left(\frac{\partial U}{\partial P}\right)_{T,n} &= 8.51 \times 10^{-4}\ \text{J atm}^{-1}.\end{aligned}$$

Estimate the change in the energy of 1.000 mol of CCl_4 if its temperature is changed from 20.0 °C to 40.0 °C and its pressure from 1.0 atm to 100.0 atm.

Since n is fixed,

$$\begin{aligned}\Delta U \approx & \ 129.4\ \text{J K}^{-1})(20.0\ \text{K}) \\ & + \left(8.51 \times 10^{-4}\ \text{J atm}^{-1}\right)(99.0\ \text{atm}) \\ = & \ 2588\ \text{J} + 0.084\ \text{J} = 2588\ \text{J}.\end{aligned}$$

Notice that the second term is negligible.

Exercise 8.1. The volume of a right circular cylinder is given by

$$V = \pi r^2 h,$$

where r is the radius and h the height. Calculate the percentage error in the volume if the radius and the height are measured and a 1.00% error is made in each measurement in the same direction. Use the formula for the differential, and direct substitution into the formula for the volume, and compare the two answers.

8.3 CHANGE OF VARIABLES

We can consider the thermodynamic energy U of a one-component, one-phase system to be a function of *T, V*, and n,

$$U = U(T, V, n) \tag{8.17}$$

or a function of *T, P*, and n,

$$U = U(T, P, n). \tag{8.18}$$

The two choices lead to different expressions for dU,

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_{V,n}\mathrm{d}T + \left(\frac{\partial U}{\partial P}\right)_{T,n}\mathrm{d}V + \left(\frac{\partial U}{\partial n}\right)_{T,V}\mathrm{d}n \tag{8.19}$$

and

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_{P,n} \mathrm{d}T + \left(\frac{\partial U}{\partial P}\right)_{T,n} \mathrm{d}P + \left(\frac{\partial U}{\partial n}\right)_{T,P} \mathrm{d}n. \tag{8.20}$$

There are two different derivatives of U with respect to T: $(\partial U/\partial T)_{V,n}$ and $(\partial U/\partial T)_{P,n}$. For most systems, these derivatives do not have the same value, so it important that we include the subscripts.

Example 8.3. Express the function $z = x(x,y) = ax^2 + bxy + cy^2$ in terms of x and u, where $u = xy$. Find the two partial derivatives $(\partial z/\partial x)_y$ and $(\partial z/\partial x)_u$.

$$\begin{aligned} z &= z(x,u) = ax^2 + bu + \frac{cu^2}{x^2}, \\ \left(\frac{\partial z}{\partial x}\right)_y &= \left[\frac{\partial}{\partial x}\left(ax^2 + bxy + y^2\right)\right]_y = 2ax + by, \\ \left(\frac{\partial z}{\partial x}\right)_u &= \left[\frac{\partial}{\partial x}\left(ax^2 + bu + \frac{cu^2}{x^2}\right)\right]_u = 2ax - \frac{2cu^2}{x^3}, \\ &= \left(\frac{\partial z}{\partial x}\right)_y - \frac{bu}{x} - \frac{2cu^2}{x^3}. \end{aligned}$$

8.4 USEFUL PARTIAL DERIVATIVE IDENTITIES

It is fairly common in thermodynamics to have measured values for some partial derivative such as $(\partial H/\partial T)_{P,n}$, which is equal to the heat capacity at constant pressure. However, some other partial derivatives are difficult or impossible to measure. It is convenient to be able to express such partial derivatives in terms of measurable quantities. We now obtain some identities that can be used for this purpose.

8.4.1 The Variable-Change Identity

In the previous example, we had the formula to represent the mathematical function. In thermodynamics, it is unusual to have a functional form. We will obtain a formula of the type

$$\left(\frac{\partial U}{\partial T}\right)_{V,n} = \left(\frac{\partial U}{\partial T}\right)_{P,n} + ? \tag{8.21}$$

where the question mark indicates a term that we need to find. The procedure that we use is not mathematically acceptable, but it does give the correct answer. To construct the partial derivative on the left-hand side of our equation, we begin with an expression for the differential $\mathrm{d}U$ that contains the derivative on the right-hand side. This is the same as Eq. (8.20). We "divide" this differential expression by $\mathrm{d}T$, specifying that we keep V and n constant, because the derivative we want on the left-hand side is $(\partial U/\partial T)_{V,n}$. This "division" cannot be done legitimately, because $\mathrm{d}T$ is an infinitesimal quantity, but it will lead to the correct answer. We get

$$\frac{\mathrm{d}U}{\mathrm{d}T} = \left(\frac{\partial U}{\partial T}\right)_{P,n} \frac{\mathrm{d}T}{\mathrm{d}T} + \left(\frac{\partial U}{\partial P}\right)_{T,n} \frac{\mathrm{d}P}{\mathrm{d}T} + \left(\frac{\partial U}{\partial n}\right)_{P,T} \frac{\mathrm{d}n}{\mathrm{d}T}. \tag{8.22}$$

We interpret the "quotients" as partial derivatives, since we have specified that we want to have V and n constant. The same variables must be held fixed in all four of the partial derivatives to keep a valid equation. We now write

$$\begin{aligned} \left(\frac{\partial U}{\partial T}\right)_{V,n} = &\left(\frac{\partial U}{\partial T}\right)_{P,n}\left(\frac{\partial T}{\partial T}\right)_{V,n} + \left(\frac{\partial U}{\partial P}\right)_{T,n}\left(\frac{\partial P}{\partial T}\right)_{V,n} \\ &+ \left(\frac{\partial U}{\partial n}\right)_{P,T}\left(\frac{\partial n}{\partial T}\right)_{V,n}. \end{aligned} \tag{8.23}$$

The partial derivative of T with respect to T is equal to unity, no matter what is held constant, and the partial derivative of n with respect to anything is zero if n is constant, so we have

$$\boxed{\left(\frac{\partial U}{\partial T}\right)_{V,n} = \left(\frac{\partial U}{\partial T}\right)_{P,n} + \left(\frac{\partial U}{\partial P}\right)_{T,n}\left(\frac{\partial P}{\partial T}\right)_{V,n}}. \tag{8.24}$$

Equation (8.24) is an example of the *variable-change identity*. If each symbol is consistently replaced by another symbol, we will have a useful equation for other variables besides the thermodynamic energy.

Example 8.4. Apply the foregoing method to the function in Example 8.2 and find the relation between $(\partial z/\partial x)_u$, and $(\partial z/\partial x)_y$.

$$\left(\frac{\partial z}{\partial x}\right)_u = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_u,$$

$$\left(\frac{\partial z}{\partial y}\right)_x = bx + 2cy = bx + \frac{2cu}{x},$$

$$\left(\frac{\partial y}{\partial x}\right)_u = \left[\frac{\partial}{\partial x}\left(\frac{u}{x}\right)\right]_u = -\frac{u}{x^2},$$

$$\left(\frac{\partial z}{\partial x}\right)_u = \left(\frac{\partial z}{\partial x}\right)_y - \frac{bu}{x} - \frac{2cu}{x^3}.$$

This agrees with Example 8.2, as it must.

Exercise 8.2. Complete the following equations.

(a) $\left(\frac{\partial H}{\partial T}\right)_{P,n} = \left(\frac{\partial H}{\partial T}\right)_{V,n} + ?$

(b) $\left(\frac{\partial z}{\partial u}\right)_{x,y} = \left(\frac{\partial z}{\partial u}\right)_{x,w} + ?$

(c) Apply the equation of part b if $z = \cos\left(x/u\right) + 4y/u$ and $w = y/u$.

8.4.2 The Reciprocal Identity

The *reciprocal identity* states that a derivative is equal to the reciprocal of the derivative with the roles of dependent and independent variables reversed:

$$\boxed{\left(\frac{\partial y}{\partial x}\right)_{z,u} = \frac{1}{(\partial x/\partial y)_{z,u}}}. \tag{8.25}$$

The same variables must be held constant in the two derivatives.

Example 8.5. Show that

$$\left(\frac{\partial P}{\partial V}\right)_{n,T} = \frac{1}{(\partial V/\partial P)_{n,T}}$$

for an ideal gas.

$$\left(\frac{\partial P}{\partial V}\right)_{n,T} = -\frac{nRT}{V^2},$$

$$\frac{1}{(\partial V/\partial P)_{n,T}} = \frac{1}{-nRT/P^2} = -\frac{P^2}{nRT}$$
$$= -\frac{(nRT/V)^2}{nRT} = -\frac{nRT}{V^2}.$$

Exercise 8.3. Show that the reciprocal identity is satisfied by $(\partial z/\partial x)_y$ and $(\partial x/\partial z)_y$ if

$$z = \sin\left(\frac{x}{y}\right) \quad \text{and} \quad x = y\sin^{-1}(z) = y\arcsin(z).$$

8.4.3 The Euler Reciprocity Relation

There are two kinds of *second partial derivatives*. If $z = z(x,y)$ we can differentiate twice with respect to x:

$$\left(\frac{\partial^2 z}{\partial x^2}\right) = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial x}\right)_y\right]_y. \tag{8.26}$$

In this case, y is held fixed in both differentiations. In addition, we can also differentiate once with respect to x and once with respect to y. This produces a *mixed second partial derivative*.

$$\boxed{\frac{\partial^2 z}{\partial y \partial x} = \left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x}. \tag{8.27}$$

In the symbol on the left, the independent variable on the right operates first. Since both variables are shown in the symbol, the subscripts are usually omitted, as in the symbol on the left. However, if there is a third independent variable, it must be held constant and is listed as a subscript. For example,

$$\left(\frac{\partial^2 U}{\partial V\,\partial T}\right)_n = \left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_{V,n}\right]_{T,n}. \tag{8.28}$$

It is possible to differentiate in the other order. The *Euler reciprocity relation* is an identity relating the two mixed second partial derivatives. It was proved by Euler[1] that the two different mixed second partial derivatives must equal each other:

$$\boxed{\frac{\partial^2 z}{\partial y\,\partial x} = \frac{\partial^2 z}{\partial x\,\partial y}}. \tag{8.29}$$

Example 8.6. Show that $(\partial^2 P/\partial V\,\partial T)_n = (\partial^2 P/\partial T\,\partial V)_n$ for an ideal gas.

$$\left(\frac{\partial^2 P}{\partial V\,\partial T}\right)_n = \left[\frac{\partial}{\partial V}\left(\frac{nR}{V}\right)\right]_{T,n} = -\frac{nR}{V^2},$$

$$\left(\frac{\partial^2 P}{\partial T\,\partial V}\right)_n = \left[\frac{\partial}{\partial T}\left(\frac{nRT}{V^2}\right)\right]_{V,n} = -\frac{nR}{V^2}.$$

Exercise 8.4. Show by differentiation that $(\partial^2 z/\partial y\,\partial x) = (\partial^2 z/\partial x\,\partial y)$ if

$$z = e^{xy}\sin(x).$$

8.4.4 The Maxwell Relations

An important set of identities obtained from the Euler reciprocity relation and thermodynamic equations is the set of *Maxwell relations*.[2] These relations allow you to replace a partial derivative that is difficult or impossible to measure with one that can be measured. One of the Maxwell relations is obtained from the thermodynamic relation

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V, \tag{8.30}$$

which holds for reversible changes in a closed system (one with fixed value of n, the amount of substance in the system). Use of the Euler reciprocity relation gives

$$\left(\frac{\partial T}{\partial V}\right)_{S,n} = -\left(\frac{\partial P}{\partial S}\right)_{V,n}. \tag{8.31}$$

Another relation is

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial P}{\partial T}\right)_{V,n}.$$

[1] Leonhard Euler (1707–1783) was a great Swiss mathematician who made many contributions. The letter "e" was chosen for the base of natural logarithms in his honor.

[2] James Clerk Maxwell (1831–1879) was a great Scottish physicist who made contributions to thermodynamics, but whose greatest contribution was the Maxwell equations of electromagnetism.

This relation can be used to replace $\left(\frac{\partial S}{\partial V}\right)_{T,n}$ by $\left(\frac{\partial P}{\partial T}\right)_{V,n}$, which is much more easily measured. There is a mnemonic device that can be used to construct other Maxwell relations: Write S and T in opposite corners of the relation, and P and V in the other opposite corners. There are four ways to do this. Keep n fixed on both sides, and on each side keep the independent variable fixed that is differentiated on the other side. If T and V occur in the same derivative, insert a negative sign on one side.

Example 8.7. Find an expression for $(\partial S/\partial V_{T,n})$ for an ideal gas.

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{nR}{V}.$$

This is an easily measured quantity.

Exercise 8.5. Using the mnemonic device, write three additional Maxwell relations.

8.4.5 The Cycle Rule

Another useful identity is the *cycle rule*

$$\boxed{\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1}. \tag{8.32}$$

Many people are at first surprised by this identity, thinking at first that the right-hand side should equal $+1$ instead of -1. We will "derive" this in the same nonrigorous way as was used to obtain Eq. (8.24). We write the differential of y as a function of x and z:

$$\mathrm{d}y = \left(\frac{\partial y}{\partial x}\right)_z \mathrm{d}x + \left(\frac{\partial y}{\partial z}\right)_x \mathrm{d}z. \tag{8.33}$$

This equation delivers the value of dy corresponding to arbitrary infinitesimal changes in x and z, so it is still correct if we choose values of dz and dx such that dy vanishes. We now "divide" nonrigorously by dx, and interpret the "quotients" of differentials as partial derivatives, remembering that y is held fixed by our choice that dy vanishes,

$$\begin{aligned} 0 &= \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial x}\right)_y + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \\ &= \left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y. \end{aligned} \tag{8.34}$$

We have used the fact that the partial derivative of x with respect to x is equal to unity. We multiply both terms of this equation by $(\partial x/\partial y)_z$ and apply the reciprocal identity:

$$0 = 1 + \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x. \tag{8.35}$$

Our derivation is indefensible, but the result is correct.

Example 8.8. For the function $y = z\ln(x)$, show that the cycle rule is valid.

$$\begin{aligned} (\partial y/\partial x)_z &= z/x, \\ (\partial x/\partial z)_y &= e^{y/z}(-\frac{y}{x^2}), \\ (\partial z/\partial y)_x &= 1/\ln(x), \end{aligned}$$

$$\begin{aligned} (\partial y/\partial x)_z(\partial x/\partial z)_y(\partial z/\partial y)_x &= (z/x)e^{y/z}\left(-\frac{y}{x^2}\right)(1/\ln(x)) \\ &= -\left(\frac{1}{x}\right)e^{y/z}\left(\frac{y}{z}\right)\left(\frac{1}{\ln(x)}\right) \\ &= -\left(\frac{1}{x}\right)e^{y/z} = -\frac{x}{x} = -1. \end{aligned}$$

Exercise 8.6. For the function $y = x^2/z$, show that the cycle rule is valid.

8.4.6 The Chain Rule

The *chain rule* involves a variable that is a function of an independent variable that itself is a function of another variable. If $z = z(u,x,y)$ but if x can be expressed as a function of u, v, and y, then

$$\boxed{\left(\frac{\partial z}{\partial y}\right)_{u,v} = \left(\frac{\partial z}{\partial x}\right)_{u,v}\left(\frac{\partial x}{\partial y}\right)_{u,v}}. \tag{8.36}$$

This is very similar to Eq. (6.20). Notice that the same variables must be held fixed in all three derivatives.

Example 8.9. Show that if $z = ax^2 + bwx$ and $x = uy$ then Eq. (8.36) is valid.

$$\left(\frac{\partial z}{\partial x}\right)_{u,w}\left(\frac{\partial x}{\partial y}\right)_{u,w} = (2ax + bw)(u) = 2au^2y + buw,$$

$$\left(\frac{\partial z}{\partial y}\right)_{u,w} = \left[\frac{\partial}{\partial y}\left(au^2y^2 + bwuy\right)\right]_{u,w} = 2au^2y + buw.$$

Exercise 8.7. Show that if $z = ax^3 + b\sin(x)$ and $x = cy$ then the chain rule is valid.

8.5 THERMODYNAMIC VARIABLES RELATED TO PARTIAL DERIVATIVES

The following are commonly measured quantities that are related to partial derivatives:

- Heat capacity at constant pressure

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{P,n} = T\left(\frac{\partial S}{\partial T}\right)_{P,n}.$$

- Heat capacity at constant volume

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,n} = T\left(\frac{\partial S}{\partial T}\right)_{V,n}.$$

- Isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n}.$$

- Adiabatic compressibility

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,n}.$$

- Coefficient of thermal expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,n}.$$

In these equations, U represents the thermodynamic energy, H represents the enthalpy, defined by

$$H = U + PV$$

and S represents the entropy, defined only through its differential

$$\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{rev}}}{T},$$

where $\mathrm{d}q_{\mathrm{rev}}$ represents an infinitesimal amount of heat transferred to a system in a reversible process. There are a number of useful relationships among these quantities.

Example 8.10. Show that $C_P/C_V = \kappa_T/\kappa_S$.

Using the cycle rule on the numerator and the denominator,

$$\frac{C_P}{C_V} = \frac{\left(\frac{\partial S}{\partial T}\right)_{P,n}}{\left(\frac{\partial S}{\partial T}\right)_{V,n}} = \frac{-\left(\frac{\partial S}{\partial P}\right)_{T,n}\left(\frac{\partial P}{\partial T}\right)_{S,n}}{-\left(\frac{\partial S}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{S,n}}.$$

We use the reciprocal identity twice to write

$$\frac{C_P}{C_V} = \frac{\left(\frac{\partial S}{\partial P}\right)_{T,n}\left(\frac{\partial V}{\partial S}\right)_{T,n}}{\left(\frac{\partial T}{\partial P}\right)_{S,n}\left(\frac{\partial V}{\partial T}\right)_{S,n}}.$$

By the chain rule

$$\frac{C_P}{C_V} = \frac{\left(\frac{\partial V}{\partial P}\right)_{T,n}}{\left(\frac{\partial V}{\partial P}\right)_{S,n}} = \frac{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n}}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,n}} = \frac{\kappa_T}{\kappa_S}.$$

8.6 EXACT AND INEXACT DIFFERENTIALS

The differential of a function is called an *exact differential*. There can also be differential forms that are not differentials of any function. A general *differential form* or *Pfaffian form* in terms of $\mathrm{d}x$ and $\mathrm{d}y$ can be written

$$\mathrm{d}u = M(x,y)\mathrm{d}x + N(x,y)\mathrm{d}y, \tag{8.37}$$

where M and N are functions of x and y. If this is the differential of a function, then M and N must be the appropriate partial derivatives of that function. If M and N are not the appropriate partial derivatives of the same function, $\mathrm{d}u$ is called an *inexact differential*. It is an infinitesimal quantity that can be calculated from specified infinitesimal values of $\mathrm{d}x$ and $\mathrm{d}y$, but it is not equal to the change in any function of x and y resulting from these changes.

In order to tell whether some differential form is an exact differential or not, we apply the Euler reciprocity relation. If there exists a function $u = u(x,y)$ such that

$$M(x,y) = \left(\frac{\partial u}{\partial x}\right)_y \quad \text{and} \quad N(x,y) = \left(\frac{\partial u}{\partial y}\right)_x, \tag{8.38}$$

then from the Euler reciprocity relation,

$$\frac{\partial^2 u}{\partial x\,\partial y} = \frac{\partial^2 u}{\partial y\,\partial x}, \tag{8.39}$$

which means that if the differential is exact

$$\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial M}{\partial y}\right)_x \quad \text{(exact differential)}, \tag{8.40}$$

Equation (8.40) represents a necessary and sufficient condition for the differential of Eq. (8.37) to be exact. That is, if the differential is exact, Eq. (8.40) will be obeyed, and if Eq. (8.40) is obeyed, the differential is exact.

Example 8.11. Show that the following differential is exact:

$$\mathrm{d}z = \left(2xy + \frac{9x^2}{y}\right)\mathrm{d}x + \left(x^2 - \frac{3x^2}{y^2}\right)\mathrm{d}y,$$

$$\left[\frac{\partial}{\partial y}\left(2xy + \frac{9x^2}{y}\right)\right]_x = 2x - \frac{9x^2}{y^2},$$

$$\left[\frac{\partial}{\partial x}\left(x^2 - \frac{3x^3}{y^2}\right)\right]_x = 2x - \frac{9x^2}{y^2}.$$

Exercise 8.8. Determine whether the following differential is exact.

$$\mathrm{d}u = (2ax + by^2)\mathrm{d}x + (bxy)\mathrm{d}y.$$

Differential forms with three or more terms can also either be exact or inexact. The Euler reciprocity relation provides a test for such differentials. For example, if

$$\mathrm{d}u = M(x,v,z)\mathrm{d}x + N(x,y,z)\mathrm{d}y + P(x,y,z)\mathrm{d}z, \quad (8.41)$$

then in order for this to be an exact differential, the three equations must be obeyed:

$$\left(\frac{\partial M}{\partial y}\right)_{x,z} = \left(\frac{\partial N}{\partial x}\right)_{y,z}, \quad (8.42)$$

$$\left(\frac{\partial N}{\partial z}\right)_{x,y} = \left(\frac{\partial P}{\partial y}\right)_{x,z}, \quad (8.43)$$

$$\left(\frac{\partial M}{\partial z}\right)_{x,y} = \left(\frac{\partial P}{\partial x}\right)_{y,z}. \quad (8.44)$$

Exercise 8.9. Show that the following is not an exact differential $\mathrm{d}u = (2y)\mathrm{d}x + (x)\mathrm{d}y + \cos(z)\mathrm{d}z$.

There are two important inexact differentials in thermodynamics. Assume that a closed equilibrium system undergoes an infinitesimal reversible process (one in which the system remains at equilibrium). We denote the amount of heat transferred to the system by $\mathrm{d}q_{\mathrm{rev}}$ and denote the amount of work done on the system by $\mathrm{d}w_{\mathrm{rev}}$. Thermodynamic theory implies that if no work is done except by changing the volume of the system, then

$$\mathrm{d}w_{\mathrm{rev}} = -P\,\mathrm{d}V, \quad (8.45)$$

where P is the pressure of the system and V is its volume.

Example 8.12. Show that for an ideal gas undergoing a reversible process with n fixed, $\mathrm{d}w_{\mathrm{rev}}$ is inexact.

We choose T and V as our independent variables and write the differential form

$$\mathrm{d}w = M\,\mathrm{d}T + N\,\mathrm{d}V \quad (n \text{ fixed}).$$

Comparison with Eq. (8.45) shows that $M = 0$ *and* $N = -P = -nRT/V$. We apply the test for exactness, Eq. (8.40), using the fact that n is constant

$$\left(\frac{\partial M}{\partial V}\right)_{T,n} = 0,$$

$$\left(\frac{\partial N}{\partial T}\right)_{V,n} = \left[\frac{\partial}{\partial T}\left(-\frac{nRT}{V}\right)\right]_{V,n} = -\frac{nR}{V} \neq 0.$$

In thermodynamics, quantities such as the thermodynamic energy, the volume, the pressure, the temperature, the amount of substances, and so forth, are functions of the variables that can be used to specify the state of the system. They are called *state functions* or *state variables*. The differentials of these quantities are exact differentials. Work and heat are not state functions. There is no such thing as an amount of work or an amount of heat in a system. We have already seen that $\mathrm{d}w_{\mathrm{rev}}$ is not an exact differential. An infinitesimal amount of heat is also not an exact differential. For a system in which work is done only by changing the volume, the thermodynamic energy, U, is defined by its differential

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w.$$

The first law of thermodynamics asserts that $\mathrm{d}U$ is an exact differential even though $\mathrm{d}q$ and $\mathrm{d}w$ are not.

Exercise 8.10. The thermodynamic energy of a monatomic ideal gas is given by

$$U = \frac{3nRT}{2}.$$

Find the partial derivatives and write the expression for $\mathrm{d}U$ using T, V, and n as independent variables. Show that your differential is exact.

8.6.1 Integrating Factors

Some inexact differentials produce exact differentials if the inexact differential is multiplied by a function called an *integrating factor.*

Example 8.13. Show that the differential

$$\mathrm{d}u = M\,\mathrm{d}x + N\,\mathrm{d}y = (2ax^2 + bxy)\mathrm{d}x + (bx^2 + 2cxy)\mathrm{d}y$$

is inexact, but that $1/x$ is an integrating factor, so that $\mathrm{d}u/x$ is exact.

We first show that $\mathrm{d}u$ is inexact:

$$\left[\frac{\partial}{\partial y}(2ax^2 + bxy)\right]_x = bx,$$

$$\left[\frac{\partial}{\partial x}(bx^2 + 2cxy)\right]_y = 2bx + 2cy \neq bx,$$

so $\mathrm{d}u$ is inexact. After we divide by x, we obtain the partial derivatives

$$\left[\frac{\partial}{\partial y}\left(\frac{M}{x}\right)\right]_x = \left[\frac{\partial}{\partial y}(2ax + by)\right]_x = b,$$

$$\left[\frac{\partial}{\partial x}\left(\frac{N}{x}\right)\right]_y = \left[\frac{\partial}{\partial x}(bx + 2cy)\right]_y = b,$$

so $(1/x)\mathrm{d}u$ is exact.

Exercise 8.11. Show that the differential

$$(1+x)\mathrm{d}x + \left[\frac{x\ln(x)}{y} + \frac{x^2}{y}\right]\mathrm{d}y$$

is inexact, and that y/x is an integrating factor.

The second law of thermodynamics asserts that even though dq_{rev} is not exact, the reciprocal of the Kelvin temperature is an integrating factor:

$$dS = \frac{dq_{rev}}{T},$$

so that dS, the differential of the entropy, is exact.

There is no general method for finding an integrating factor, although we will discuss a method that will work for a particular class of differential forms in Chapter 8, when we discuss differential equations. However, it is true that if a differential possesses one integrating factor, there are infinitely many integrating factors for that differential.

8.7 MAXIMUM AND MINIMUM VALUES OF FUNCTIONS OF SEVERAL VARIABLES

A point at which either a maximum or a minimum value in a function occurs is called an *extremum*. For example, Figure 8.3 shows a perspective view of a graph of the function $f = e^{-x^2-y^2}$. The surface representing the function has a "peak" at the origin, representing a maximum value of the function.

The figure also shows a curve at which the surface intersects with a plane representing the equation $y = 1 - x$. On this curve there is also a maximum, which has a smaller value than the maximum at the peak. We call this value a *constrained maximum* subject to the constraint that $y = 1 - x$. We discuss the constrained maximum later.

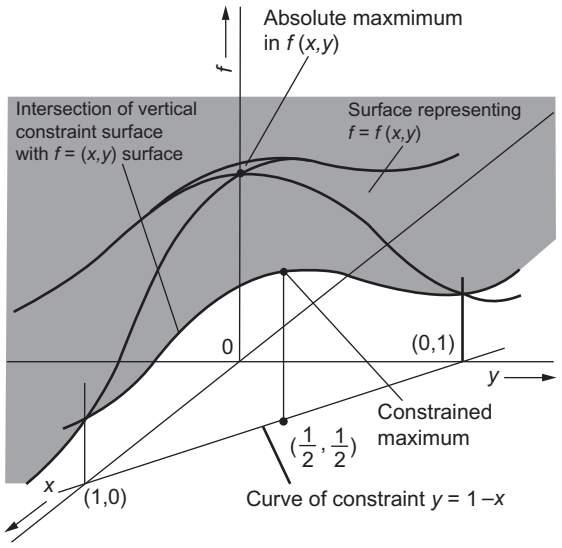

FIGURE 8.3 The surface representing the function $y = e^{-x^2-y^2}$ with the absolute maximum and a constrained maximum shown.

The maximum at the origin in Figure 8.3 is called a *local maximum* or a *relative maximum*, because the value of the function at such a peak is larger than at any other point in the immediate vicinity. However, a complicated function can have more than one local maximum. Also, if we consider a finite region, the function might have a larger value somewhere on the boundary of the region that is larger than the value at a local maximum. To find the *absolute maximum* of the function for a given region, we must consider all local maxima and any points on the boundary of the region that might have greater values. The peak at the origin in Figure 8.3 is the absolute maximum of this function. Points of minimum value are completely analogous to points of maximum value. *Local minima* are located at the bottom of depressions or valleys in the surface representing the function. To find an absolute minimum for a given region, you must consider all local minima and any points on the boundary of the region that might have smaller values.

To locate a local maximum or minimum, we use the fact that the plane that is tangent to the surface will be horizontal at any local maximum or minimum. Therefore, the curve representing the intersection of any vertical plane with the surface will have a local maximum or a local minimum at the same place. The partial derivative with respect to one independent variable gives the slope of the tangent to the curve in the plane corresponding to a constant value of the other independent variable, so we can find a local maximum or minimum by finding the places where all the partial derivatives of the function vanish simultaneously.

Our method for a differentiable function of two variables is therefore to

1. Solve the simultaneous equations

$$\left(\frac{\partial f}{\partial x}\right)_y = 0, \qquad (8.46)$$

$$\left(\frac{\partial f}{\partial y}\right)_x = 0.$$

2. Calculate the value of the function at all points satisfying these equations, and at the boundaries of the region being considered and any cusps or discontinuities. The maximum or minimum value in the region being considered must be in this set of values.

Example 8.14. Find the maximum value of the function shown in Figure 8.3, $f = e^{-x^2-y^2}$.

At a local maximum or minimum

$$\left(\frac{\partial f}{\partial x}\right)_y = e^{-x^2-y^2}(-2x) = -2xe^{-x^2-y^2},$$

$$\left(\frac{\partial f}{\partial y}\right)_x = e^{-x^2-y^2}(-2y) = 0 = -2ye^{-x^2-y^2}.$$

The only solution for finite values of x and y is $x = 0, y = 0$. Since no restricted region was specified, we consider all values of x and y. For very large magnitudes of x or y, the function vanishes, so we have found the desired absolute maximum, at which $f(0,0) = 1$.

In the case of one independent variable, a local maximum could be distinguished from a local minimum or an inflection point by determining the sign of the second derivative. With more than one variable, the situation is more complicated. In addition to inflection points, we can have points corresponding to a maximum with respect to one variable and a minimum with respect to another. Such a point is called a *saddle point*, and at such a point, the surface representing the function resembles a mountain pass or the surface of a saddle. Such points are important in the *transition-state theory* of chemical reaction rates.

For two independent variables, we calculate the following quantity:

$$D = \left(\frac{\partial^2 f}{\partial x^2}\right)\left(\frac{\partial^2 f}{\partial y^2}\right) - \left(\frac{\partial^2 f}{\partial x\,\partial y}\right)^2. \tag{8.47}$$

The different cases are as follows:

1. If $D > 0$ and $(\partial^2 f/\partial x^2) > 0$, then we have a local minimum.
2. If $D > 0$ and $(\partial^2 f/\partial x^2) < 0$, then we have a local maximum.
3. If $D < 0$, then we have neither a local maximum nor a local minimum.
4. If $D = 0$, the test fails, and we cannot tell what we have.

Exercise 8.12. Evaluate D at the point $(0,0)$ for the function of the previous example and establish that the point is a local maximum.

For more than two independent variables, the method is similar, except that there is one equation for each independent variable.

8.7.1 Constrained Maximum/Minimum Problems

Sometimes we must find a maximum or a minimum value of a function subject to some condition, which is called a *constraint*. Such an extremum is called a *constrained maximum* or a *constrained minimum*. Generally, a constrained maximum is smaller than the unconstrained maximum of the function, and a constrained minimum is larger than the unconstrained minimum of the function. Consider the following example:

Example 8.15. Find the maximum value of the function in the previous example subject to the constraint $x + y = 1$.

The constraint corresponds to the specification of y as a function of x by

$$y = 1 - x.$$

This function is given by the line in the x–y plane of Figure 8.3. We are now looking for the place along this curve at which the function has a larger value than at any other place on the curve.

Since y is a function of x on the curve, the direct way to proceed is to replace y by $1 - x$:

$$f = (x, 1-x) = f(x) = e^{-x^2-(1-x)^2} = e^{-2x^2+2x-1}.$$

Since f is now a function only of x, the local maximum is now at the point where $\mathrm{d}f/\mathrm{d}x$ vanishes:

$$\frac{\mathrm{d}f}{\mathrm{d}x} = e^{-2x^2-(1-x)^2}(-4x+2) = 0.$$

This equation is satisfied by $x = \frac{1}{2}$ and by $|x| \to \infty$. The constrained maximum corresponds to $x = \frac{1}{2}$ and the minimum corresponds to $|x| \to \infty$. At the constrained maximum $y = 1 - \frac{1}{2} = \frac{1}{2}$ and the value of the function at the constrained maximum is

$$f\left(\frac{1}{2}, \frac{1}{2}\right) = \exp\left[-\left(\frac{1}{2}^2\right) - \left(\frac{1}{2}\right)^2\right] = e^{-1/2} = 0.6065\cdots$$

As expected, this value is smaller than the unconstrained maximum, at which $f = 1$.

8.7.2 Lagrange's Method of Undetermined Multipliers[3]

If we have a constrained maximum or minimum problem with more than two variables, the direct method of substituting the constraint relation into the function might not be practical. Lagrange's method finds a constrained maximum or minimum without substituting the constraint relation into the function. If the constraint is written in the form $g(x,y) = 0$, the method for finding the constrained maximum or minimum in $f(x,y)$ is as follows:

1. Form the new function

$$u(x,y) = f(x,y) + \lambda g(x,y), \tag{8.48}$$

where λ is a constant called an *undetermined multiplier*. Its value is unknown at this point of the analysis.

[3] Named for Joseph Louis Lagrange (born Guisepps Lodovico Lagrangia), 1736–1813, French-Italian physicist and mathematician.

2. Form the partial derivatives of u, and set them equal to zero,

$$\left(\frac{\partial u}{\partial x}\right)_y = \left(\frac{\partial f}{\partial x}\right)_y + \lambda\left(\frac{\partial g}{\partial x}\right)_y = 0, \tag{8.49}$$

$$\left(\frac{\partial u}{\partial x}\right)_x = \left(\frac{\partial f}{\partial x}\right)_x + \lambda\left(\frac{\partial g}{\partial x}\right)_x = 0. \tag{8.50}$$

3. Solve the set of equations consisting of $g = 0$ and these two equations as a set of simultaneous equations for the value of x, the value of y, and the value of λ that correspond to the local maximum or minimum.

Example 8.16. Find the constrained maximum of the previous example by the method of Lagrange.

The constraint equation is written

$$g(x,y) = x + y - 1 = 0.$$

The function u is

$$u(x,y) = e^{-x^2-y^2} + \lambda(x + y - 1).$$

The three equations to be solved are

$$\left(\frac{\partial u}{\partial x}\right)_y = \left(-2x\right)e^{-x^2-y^2} + \lambda = 0,$$

$$\left(\frac{\partial u}{\partial y}\right)_x = \left(-2y\right)e^{-x^2-y^2} + \lambda = 0,$$

$$g(x,y) = x + y - 1 = 0.$$

We begin by solving for λ in terms of x and y. We multiply the first equation by y and the second equation by x and add the two equations. The result can be solved to give

$$\lambda = \frac{4xy}{x+y}e^{-x^2-y^2}.$$

Substitute this into the first equation to obtain

$$\left(-2x\right)e^{-x^2-y^2} + \frac{4xy}{x+y}e^{-x^2-y^2} = 0.$$

The exponential factor is not zero for any finite values of x and y, so

$$-2x + \frac{4xy}{x+y} = 0.$$

When the expression for λ is substituted into the second equation in the same way, the result is

$$-2y + \frac{4xy}{x+y} = 0.$$

The difference of these two equation is

$$-2x + 2y = 0,$$

which is solved for y in terms of x to obtain

$$y = x.$$

This is substituted into the third simultaneous equation to obtain

$$x + x - 1 = 0,$$

which gives

$$x = \frac{1}{2}, \quad y = \frac{1}{2}.$$

This is the same result as in the previous example. In this case, the method of Lagrange was more work than the direct method. In problems involving more variables, the method of Lagrange will usually be easier.

Exercise 8.13.

(a) Find the local minimum of the function

$$f(x,y) = x^2 + y^2 + 2x.$$

(b) Without using the method of Lagrange, find the constrained minimum subject to the constraint,

$$x = -y.$$

(c) Find the constrained minimum using the method of Lagrange.

The method of Lagrange also works if there is more than one constraint. Assume that we desire the local maximum or minimum of the function

$$f = f(x,y,z) \tag{8.51}$$

subject to the two constraints

$$g_1(x,y,z) = 0 \tag{8.52}$$

and

$$g_2(x,y,z) = 0. \tag{8.53}$$

The procedure is similar, except that two undetermined multipliers are used. One forms the function

$$u = u(x,y,z) = f(x,y,z) + \lambda_1 g_1(x,y,z) + \lambda_2 g_2(x,y,z) \tag{8.54}$$

and solves the set of simultaneous equations consisting of Eqs. (8.52) and (8.53), and the three equations:

$$\left(\frac{\partial u}{\partial x}\right)_{y,z} = 0, \tag{8.55}$$

$$\left(\frac{\partial u}{\partial y}\right)_{x,z} = 0, \tag{8.56}$$

$$\left(\frac{\partial u}{\partial z}\right)_{x,y} = 0. \tag{8.57}$$

The result is a value for λ_1, a value for λ_2, and values for x, y, and z which locate the constrained local maximum or minimum.

Example 8.17. Find the minimum in the function

$$f = x^2 + y^2 + z^2$$

subject to the constraints

$$y - 1 = 0,$$
$$z - 2 = 0.$$

We form the function

$$u = x^2 + y^2 + z^2 + \lambda_1(y-1) + \lambda_2\left(z-2\right).$$

We need to solve the equations

$$\left(\frac{\partial u}{\partial x}\right)_{y,z} = 2x = 0,$$

$$\left(\frac{\partial u}{\partial y}\right)_{x,z} = 2y + \lambda_1,$$

$$\left(\frac{\partial u}{\partial z}\right)_{x,y} = 2z + \lambda_2 = 0,$$

plus the two constraint equations. This is a simple case, since the first equation gives

$$x = 0$$

and the constraint equations give the values of y and z. The constrained minimum occurs at

$$x = 0, \quad y = 1, \quad z = 2.$$

The value of the function at this point is $f = 5$.

Exercise 8.14. Find the minimum of the previous example without using the method of Lagrange.

8.8 VECTOR DERIVATIVE OPERATORS

An *operator* is a symbol standing for one or more mathematical operations to be performed on the function represented by the symbol to the right of the operator symbol. There are several *vector derivative operators* that apply to functions of three or more variables.

8.8.1 Vector Derivatives in Cartesian Coordinates

Cartesian coordinates in three dimensions are more easily visualized than other coordinate systems, since we are naturally familiar with notions of east-west, north-south, and up-down, correlated with x, y, and z coordinates.

The Gradient

If f is some scalar function of x, y, and z, the *gradient* of f is defined in Cartesian coordinates by

$$\boxed{\nabla f = \mathbf{i}\left(\frac{\partial f}{\partial y}\right) + \mathbf{j}\left(\frac{\partial f}{\partial y}\right) + \mathbf{k}\left(\frac{\partial f}{\partial z}\right)} \left(\text{definition}\right), \tag{8.58}$$

where $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are the unit vectors in the directions of the positive ends of the x, y, and z axes, respectively. The gradient of f is sometimes denoted by grad f instead of ∇f. The symbol ∇, which is an upside-down capital Greek delta, is called "del." The gradient of a scalar function is a vector function. At any given point in three-dimensional space, the direction of the gradient of a scalar function is the direction in which the function is increasing most rapidly, and its magnitude is the rate of change of the function in that direction.

Example 8.18. Find the gradient of the function

$$f(x,y,z) = x^2 + y^2 + z^2.$$

$$\begin{aligned}\nabla f &= \mathbf{i}\left(\frac{\partial f}{\partial y}\right) + \mathbf{j}\left(\frac{\partial f}{\partial y}\right) + \mathbf{k}\left(\frac{\partial f}{\partial z}\right) \\ &= \mathbf{i}2x + \mathbf{j}2y + \mathbf{k}2z = 2(\mathbf{i}x + \mathbf{j}y + \mathbf{k}z).\end{aligned}$$

The function $f = x^2 + y^2 + z^2$ is spherically symmetric. That is, it has the same value at all points that are the same distance from the origin. At any point this gradient is a vector pointing directly away from the origin, which is the direction in which the function increases more rapidly than in any other direction.

Exercise 8.15. Find the gradient of the function

$$g(x,y,z) = ax^3 + ye^{bz},$$

where a and b are constants.

A common example of a gradient is found in classical mechanics. If the force on a particle is velocity-independent, it is given by

$$\boxed{\mathbf{F} = -\nabla \mathcal{V}}, \tag{8.59}$$

where $\mathcal{V}$ is the potential energy of the system and $\mathbf{F}$ is the force. The gradient is taken with respect to the coordinates of the particle being considered, and the coordinates of any other particles are treated as constants in the differentiations.

Example 8.19. Neglecting the attractions of all other celestial bodies, the gravitational potential energy of the earth and the sun is given by

$$\mathcal{V} = -\frac{Gm_s m_e}{r},$$

where G is the universal gravitational constant, equal to 6.673×10^{-11} m^3 s^{-2} kg^{-1}, m_s is the mass of the sun, m_e is the mass of the earth, and r is the distance from the center of the sun to the center of the earth,

$$r = \left(x^2 + y^2 + z^2\right)^{1/2}.$$

Express the force on the earth in Cartesian coordinates. That is, find the force in terms of the unit vectors **i**, **j**, and **k** with the components expressed in terms of x, y, and z.

Expressing r in terms of x, y, and z

$$\begin{aligned}
\mathbf{F} = -\nabla\mathcal{V} =& Gm_s m_e \left[\mathbf{i}\frac{\partial}{\partial x}\left(\frac{1}{\left(x^2+y^2+z^2\right)^{1/2}}\right)\right.\\
&+\mathbf{j}\frac{\partial}{\partial y}\left(\frac{1}{\left(x^2+y^2+z^2\right)^{1/2}}\right)\\
&\left.+\mathbf{k}\frac{\partial}{\partial z}\left(\frac{1}{\left(x^2+y^2+z^2\right)^{1/2}}\right)\right]\\
=& -Gm_s m_e \left[\mathbf{i}\frac{1}{2}\left(\frac{2x}{\left(x^2+y^2+z^2\right)^{3/2}}\right)\right.\\
&+\mathbf{j}\frac{1}{2}\left(\frac{2y}{\left(x^2+y^2+z^2\right)^{3/2}}\right)\\
&\left.+\mathbf{k}\frac{1}{2}\left(\frac{2z}{\left(x^2+y^2+z^2\right)^{3/2}}\right)\right]\\
=& -Gm_s m_e \left[\mathbf{i}\left(\frac{x}{\left(x^2+y^2+z^2\right)^{3/2}}\right)\right.\\
&+\mathbf{j}\left(\frac{y}{\left(x^2+y^2+z^2\right)^{3/2}}\right)\\
&\left.+\mathbf{k}\left(\frac{z}{\left(x^2+y^2+z^2\right)^{3/2}}\right)\right]\\
=& -Gm_s m_e \left[\mathbf{i}\left(\frac{x}{r^3}\right)+\mathbf{j}\left(\frac{y}{r^3}\right)+\mathbf{k}\left(\frac{z}{r^3}\right)\right]\\
=& -\frac{Gm_s m_e}{r^3}(\mathbf{i}x+\mathbf{j}y+\mathbf{k}z) = -Gm_s m_e\frac{\mathbf{r}}{r^3},
\end{aligned}$$

where **r** is the position vector $r = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z$.

Exercise 8.16. The average distance from the center of the sun to the center of the earth is 1.495×10^{11} m. The mass of the earth is 5.983×10^{24} kg, and the mass of the sun is greater than the mass of the earth by a factor of 332958. Find the magnitude of the force exerted on the earth by the sun and the magnitude of the force exerted on the sun by the earth.

The Divergence

The operator ∇ ("del") can operate on vector functions as well as on scalar functions. The gradient of a vector function has nine components, since the function has three components and the operator has three components. Such a quantity is called a *dyadic*, and we will not discuss it. We will discuss two vector derivatives, one of which is somewhat analogous to a scalar product of two vectors, and one of which is somewhat analogous to a cross product of two vectors. An example of a vector function is the velocity of a compressible flowing fluid, which depends on time as well as on position. At a fixed time, we write

$$\mathbf{v} = \mathbf{v}(x,y,z). \tag{8.60}$$

In terms of Cartesian components,

$$\mathbf{v} = \mathbf{i}v_x(x,y,z) + \mathbf{j}v_y(x,y,z) + \mathbf{k}v_z(x,y,z). \tag{8.61}$$

The *divergence* of a vector function **F** is defined in Cartesian coordinates by

$$\boxed{\nabla\cdot\mathbf{F} = \left(\frac{\partial F_x}{\partial x}\right)+\left(\frac{\partial F_y}{\partial y}\right)+\left(\frac{\partial F_z}{\partial z}\right)}\text{(definition)}, \tag{8.62}$$

where **F** is a vector function with Cartesian components F_x, F_y, and F_z. The divergence of a vector function **F** is a scalar and is somewhat analogous to a scalar product (dot product) of the del operator and a vector. The divergence of **F** is sometimes denoted by div**F**.

One way to visualize the divergence of a function is to consider the divergence of the velocity of a compressible fluid. Curves that are followed by small portions of the fluid are called *stream lines*. In a region where the stream lines diverge (become farther from each other) as the flow is followed, the fluid will become less dense, and in such a region the divergence of the velocity is positive. The divergence thus provides a measure of the spreading of the stream lines. The *equation of continuity* of a compressible fluid expresses the effect this spreading has on the density of the fluid, which depends on position and on time. The equation of continuity is written

$$\nabla\cdot(\rho\mathbf{v}) = -\frac{\partial\rho}{\partial t}, \tag{8.63}$$

where ρ is the density of the fluid, **v** is its velocity, and t is the time.

Example 8.20. Find $\nabla\cdot\mathbf{F}$ if **F** is given by

$$\mathbf{F} = \mathbf{i}x^2 + \mathbf{j}yz + \mathbf{k}\frac{xz^2}{y},$$

$$\nabla\cdot\mathbf{F} = 2x + z + \frac{2xz}{y}.$$

Exercise 8.17. Find $\nabla\cdot\mathbf{r}$ where

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z.$$

The Curl

Another derivative of a vector function is the *curl*. The curl of the vector function **F** is defined in Cartesian coordinates by

$$\boxed{\nabla \times \mathbf{F} = \mathbf{i}\left(\frac{\partial F_z}{\partial y} - \frac{\partial F_y}{\partial z}\right) + \mathbf{j}\left(\frac{\partial F_x}{\partial z} - \frac{\partial F_z}{\partial x}\right) + \mathbf{k}\left(\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y}\right)} \text{ (definition).} \tag{8.64}$$

The curl is a vector and is somewhat analogous to the vector product (cross product) of the del operator and a vector. To remember which vector derivative is which, remember that "dot" and "divergence" both begin with the letter "d" and that "cross" and "curl" both begin with the letter "c." The symbol curl**F** is sometimes used for the curl of **F**.

The curl of a vector function is more difficult to visualize than is the divergence. In fluid flow, the curl of the velocity gives the *vorticity* of the flow, or the rate of turning of the velocity vector. Because of this, the symbol rot**F** is also sometimes used for the curl of **F**.

Example 8.21. Find $\nabla \times \mathbf{F}$ if

$$\mathbf{F} = \mathbf{i}y + \mathbf{j}z + \mathbf{k}x,$$

$$\nabla \times \mathbf{F} = \mathbf{i}(0-1) + \mathbf{j}(0-1) + \mathbf{k}(0-1) = -\mathbf{i} - \mathbf{j} - \mathbf{k}.$$

Exercise 8.18. Find $\nabla \times \mathbf{r}$ if

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z.$$

Explain your result.

The Laplacian

The Laplacian is defined as the divergence of the gradient. If f is a scalar function, its gradient is a vector and the divergence of the gradient of f is a scalar. In Cartesian coordinates the Laplacian of a scalar function $f(x,y,z)$ is given by

$$\boxed{\nabla \cdot \nabla f = \nabla^2 f = \left(\frac{\partial^2 f}{\partial x^2}\right) + \left(\frac{\partial^2 f}{\partial y^2}\right) + \left(\frac{\partial^2 f}{\partial z^2}\right)} \quad \text{(definition)}. \tag{8.65}$$

The operator $\nabla \cdot \nabla$ is called, the *Laplacian operator*,[4] and has its own symbol, ∇^2, sometimes called "del squared." This operator occurs in the Schrödinger equation of quantum mechanics and in electrostatics.

[4] After Pierre Simon, Marquis de Laplace, 1749–1827, a famous French mathematician and astronomer.

Example 8.22. Find the Laplacian of the function

$$\begin{aligned} f(x,y,z) &= A\sin(ax)\sin(by)\sin(cz), \\ \nabla^2 f &= -Aa^2\sin(ax)\sin(by)\sin(cz) \\ &\quad - Ab^2\sin(ax)\sin(by)\sin(cz) \\ &\quad - Ac^2\sin(ax)\sin(by)\sin(cz) \\ &= -A\left(a^2+b^2+c^2\right)\sin(ax)\sin(by)\sin(cz) \\ &= -\left(a^2+b^2+c^2\right)f. \end{aligned}$$

Exercise 8.19. Find the Laplacian of the function

$$f = \exp(x^2+y^2+z^2) = e^{x^2}e^{y^2}e^{z^2}.$$

Two other possibilities for successive operation of the del operator are the *curl of the gradient* and the *gradient of the divergence* . The curl of the gradient of any differentiable scalar function always vanishes.

Exercise 8.20. Show that $\nabla \times \nabla f = 0$ if f is a differentiable scalar function of x, y, and z.

8.8.2 Vector Derivatives in Other Coordinate Systems

Coordinate systems such as spherical polar or cylindrical polar coordinates are called *orthogonal coordinates*, because an infinitesimal displacement produced by changing only one of the coordinates is perpendicular (orthogonal) to a displacement produced by an infinitesimal change in any one of the other coordinates. Figure 8.4 shows displacements, drawn as though they were finite, produced by positive infinitesimal changes in the spherical polar coordinates r, θ, and ϕ. These displacements are denoted by $\mathrm{d}s_r$, $\mathrm{d}s_\theta$, and $\mathrm{d}s_\phi$, and each one has the dimension of length.

$$\mathrm{d}s_r = \text{displacement in } r \text{ direction} = \mathrm{d}r, \tag{8.66}$$

$$\mathrm{d}s_\theta = \text{displacement in } \theta \text{ direction} = r\,\mathrm{d}\theta, \tag{8.67}$$

$$\mathrm{d}s_\phi = \text{displacement in } \phi \text{ direction} = r\sin(\phi)\,\mathrm{d}\theta. \tag{8.68}$$

We define three vectors of unit length in directions of the infinitesimal displacements in Figure 8.4, called $\mathbf{e_r}, \mathbf{e}_\theta$, and $\mathbf{e}_\phi$.

An infinitesimal vector displacement is the vector sum of displacements in the three orthogonal directions. In Cartesian coordinates,

$$\mathrm{d}\mathbf{r} = \mathbf{i}\,\mathrm{d}x + \mathbf{j}\,\mathrm{d}y + \mathbf{k}\,\mathrm{d}z. \tag{8.69}$$

In spherical polar coordinates,

$$\mathrm{d}\mathbf{r} = \mathbf{e_r}\mathrm{d}r + \mathbf{e}_\theta r\,\mathrm{d}\theta + \mathbf{e}_\phi r\sin(\theta)\,\mathrm{d}\theta. \tag{8.70}$$

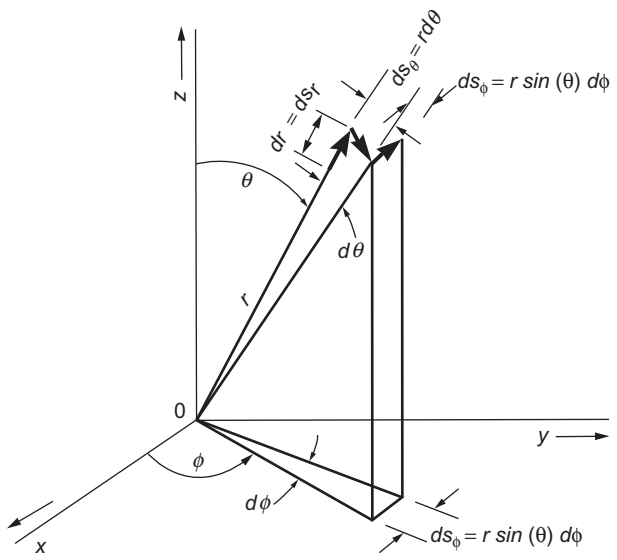

FIGURE 8.4 Infinitesimal displacements ds_r, ds_θ, and ds_ϕ produced by infinitesimal increments dr, $d\theta$, and $d\phi$.

We can write an expression for an infinitesimal vector displacement $d\mathbf{r}$ in a form that will hold for any set of orthogonal coordinates. Let the three coordinates of an orthogonal system in three dimensions be called q_1,q_2, and q_3. Let the displacements due to the infinitesimal increments be called ds_1,ds_2, and ds_3. Let the unit vectors in the directions of the displacements be called $\mathbf{e}_1$,$\mathbf{e}_2$, and $\mathbf{e}_3$. The equation analogous to Eq. (8.70) is

$$d\mathbf{r} = \mathbf{e}_1\, ds_1 + \mathbf{e}_2\, ds_2 + \mathbf{e}_3\, ds_3 = \mathbf{e}_1\, h_1\, dq_1 + \mathbf{e}_2\, h_2\, dq_2 + \mathbf{e}_3\, h_3\, dq_3, \tag{8.71}$$

where the h's are the factors needed to give the correct expression for each displacement. For Cartesian coordinates, all three of the h factors are equal to unity. For spherical polar coordinates, $h_r = 1, h_\theta = r$, and $h_\phi = r\sin(\theta)$. For other systems, you can figure out what the h's are geometrically so that $ds_i = h_i\, dq_i$ for each coordinate.

The Gradient

The gradient of a scalar function f is written in terms of components in the direction of $\mathbf{e}_1$,$\mathbf{e}_2$, and $\mathbf{e}_3$ as

$$\nabla f = \mathbf{e}_1 \frac{\partial f}{\partial s_1} + \mathbf{e}_2 \frac{\partial f}{\partial s_2} + \mathbf{e}_3 \frac{\partial f}{\partial s_3} \tag{8.72}$$

or

$$\boxed{\nabla f = \mathbf{e}_1 \frac{1}{h_1}\frac{\partial f}{\partial q_1} + \mathbf{e}_2 \frac{1}{h_2}\frac{\partial f}{\partial q_2} + \mathbf{e}_3 \frac{1}{h_3}\frac{\partial f}{\partial q_3}}. \tag{8.73}$$

The expression for the gradient of a function of spherical polar coordinates is

$$\nabla f = \mathbf{e}_\mathbf{r} \frac{\partial f}{\partial r} + \mathbf{e}_\theta \frac{1}{r}\frac{\partial f}{\partial \theta} + \mathbf{e}_\phi \frac{1}{r\sin(\theta)}\frac{\partial f}{\partial \phi}. \tag{8.74}$$

Exercise 8.21.

(a) Find the h factors for cylindrical polar coordinates.
(b) Find the expression for the gradient of a function of cylindrical polar coordinates, $f = f(\rho,\phi,z)$.
(c) Find the gradient of the function

$$f = e^{-(\rho^2+z^2)/a^2}\sin(\phi).$$

The Divergence

The *divergence of a vector function* can similarly be expressed in orthogonal coordinates. If $\mathbf{F}$ is a vector function, it must be expressed in terms of the unit vectors of the coordinate system in which we are to differentiate,

$$\mathbf{F} = \mathbf{e}_1 F_1 + \mathbf{e}_2 F_2 + \mathbf{e}_3 F_3. \tag{8.75}$$

The components F_1,F_2, and F_3 are the components in the directions of $\mathbf{e}_1$,$\mathbf{e}_2$, and $\mathbf{e}_3$.

The divergence of the vector function $\mathbf{F}$ is given by

$$\boxed{\nabla\cdot\mathbf{F} = \frac{1}{h_1h_2h_3}\left[\frac{\partial}{\partial q_1}(F_1h_2h_3) + \frac{\partial}{\partial q_2}(F_2h_1h_3) + \frac{\partial}{\partial q_3}(F_3h_1h_2)\right]}. \tag{8.76}$$

Example 8.23.

(a) Write the expression for the divergence of a vector function F expressed in terms of spherical polar coordinates.

$$\begin{aligned}\nabla\cdot\mathbf{F} &= \frac{1}{r^2\sin(\theta)}\left[\frac{\partial}{\partial r}\left[F_r r^2\sin(\theta)\right] + \frac{\partial}{\partial\theta}\left[F_\theta r\sin(\theta)\right] + \frac{\partial}{\partial\phi}(F_\phi r)\right]\\ &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2F_r\right) + \frac{1}{r\sin(\theta)}\frac{\partial}{\partial\theta}\left[\sin(\theta)\,F_\theta\right] + \frac{1}{r\sin(\theta)}\frac{\partial F_\phi}{\partial\phi}.\end{aligned}$$

(b) Find the divergence of the position vector, which in spherical polar coordinates is

$$\mathbf{r} = \mathbf{e}_\mathbf{r} r.$$
$$\nabla\cdot\mathbf{r} = \frac{1}{r^2}3r^2 + 0 + 0 = 3.$$

Exercise 8.22. Write the formula for the divergence of a vector function $\mathbf{F}$ expressed in terms of cylindrical polar coordinates. Note that $\mathbf{e}_z$ is the same as $\mathbf{k}$.

The Curl

The *curl* of a vector function **F** is defined by

$$\begin{aligned}\nabla \times \mathbf{F} = \mathbf{e}_1 \frac{1}{h_2 h_3}\left[\frac{\partial}{\partial q_2}\left(h_3 F_3\right) - \frac{\partial}{\partial q_3}\left(h_2 F_2\right)\right] \\ + \mathbf{e}_2 \frac{1}{h_1 h_3}\left[\frac{\partial}{\partial q_3}\left(h_1 F_1\right) - \frac{\partial}{\partial q_1}\left(h_3 F_3\right)\right] \\ + \mathbf{e}_3 \frac{1}{h_1 h_2}\left[\frac{\partial}{\partial q_1}\left(h_2 F_2\right) - \frac{\partial}{\partial q_2}\left(h_1 F_1\right)\right].\end{aligned} \tag{8.77}$$

In spherical polar coordinates

$$\begin{aligned}\nabla \times \mathbf{F} = \mathbf{e}_\mathbf{r} \frac{1}{r^2 \sin(\theta)}\left[\frac{\partial}{\partial \theta}\left(r \sin(\theta) F_\phi\right) - \frac{\partial}{\partial \theta}\left(r F_\theta\right)\right] \\ + \mathbf{e}_\theta \frac{1}{r \sin(\theta)}\left[\frac{\partial}{\partial \phi}\left(F_r\right) - \frac{\partial}{\partial r}\left(r \sin(\theta) F_\phi\right)\right] \\ + \mathbf{e}_\phi \frac{1}{r}\left[\frac{\partial}{\partial r}\left(r F_\theta\right) - \frac{\partial}{\partial \theta}\left(F_r\right)\right].\end{aligned} \tag{8.78}$$

Example 8.24. Find the curl of the function $F = \mathbf{e}_\mathbf{r} \sin(\phi)$

$$\begin{aligned}\nabla \times \mathbf{e}_\mathbf{r} \sin(\phi) &= \mathbf{e}_\theta \frac{1}{r \sin(\theta)}\left[\frac{\partial}{\partial \phi} \sin(\phi)\right] \\ &\quad - \mathbf{e}_\phi \frac{1}{r}\left[\frac{\partial}{\partial \theta} \sin(\phi)\right] \\ &= \mathbf{e}_\theta \frac{\cos(\phi)}{r \sin(\theta)}.\end{aligned}$$

The Laplacian

The expression for the Laplacian of a scalar function, f, is

$$\boxed{\begin{aligned}\nabla^2 f = \frac{1}{h_1 h_2 h_3}\left[\frac{\partial}{\partial q_1}\left(\frac{h_2 h_3}{h_1}\frac{\partial f}{\partial q_1}\right)\right. \\ \left. + \frac{\partial}{\partial q_2}\left(\frac{h_1 h_3}{h_2}\frac{\partial f}{\partial q_2}\right) + \frac{\partial}{\partial q_3}\left(\frac{h_1 h_2}{h_3}\frac{\partial f}{\partial q_3}\right)\right]\end{aligned}}. \tag{8.79}$$

In spherical polar coordinates

$$\boxed{\begin{aligned}\nabla^2 f = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial f}{\partial r}\right) + \frac{1}{r^2 \sin(\theta)}\frac{\partial}{\partial \theta}\left[\sin(\theta)\frac{\partial f}{\partial \theta}\right] \\ + \frac{1}{r^2 \sin^2(\theta)}\frac{\partial^2 f}{\partial \phi^2}\end{aligned}}. \tag{8.80}$$

Example 8.25. Write the expression for the Laplacian in cylindrical polar coordinates For cylindrical polar coordinates, $h_r = 1, h_\phi = r$, and $h_z = 1$.

$$\nabla^2 f = \frac{1}{r}\left[\frac{\partial}{\partial r}\left(r\frac{\partial f}{\partial r}\right) + \frac{\partial}{\partial \phi}\left(\frac{1}{r}\frac{\partial f}{\partial \phi}\right) + \frac{\partial}{\partial z}\left(r\frac{\partial f}{\partial z}\right)\right].$$

Exercise 8.23. Write the expression for the Laplacian of the function e^{-r^2}.

PROBLEMS

1. A certain nonideal gas is described by the equation of state

$$\frac{P V_\mathrm{m}}{RT} = 1 + \frac{B_2}{V_\mathrm{m}},$$

where T is the temperature on the Kelvin scale, V_m is the molar volume, P is the pressure, and R is the gas constant. For this gas, the *second virial coefficient* B_2 is given as a function of T by

$$B_2 = \left[-1.00 \times 10^{-4} - \left(2.148 \times 10^{-6}\right) \times e^{(1956\mathrm{K})/T}\right] \mathrm{m}^3\ \mathrm{mol}^{-1}.$$

Find $(\partial P/\partial V_\mathrm{m})_T$ and $(\partial P/\partial T)_{V_\mathrm{m}}$ and an expression for $\mathrm{d}P$.

2. For a certain system, the thermodynamic energy U is given as a function of S, V,and n by

$$U = U(S,V,n) = K n^{5/3} V^{-2/3} e^{2S/3nR},$$

where S is the entropy, V is the volume, n is the number of moles, K is a constant, and R is the gas constant.

(a) According to thermodynamic theory, $T = (\partial U/\partial S)_{V,n}$. Find an expression for $(\partial U/\partial S)_{V,n}$.
(b) According to thermodynamic theory, the pressure $P = -(\partial U/\partial V)_{S,n}$. Find an expression for $(\partial U/\partial V)_{S,n}$.
(c) Find an expression for $(\partial U/\partial n)_{S,V}$.
(d) Find $\mathrm{d}U$ in terms of $\mathrm{d}S, \mathrm{d}V$, and $\mathrm{d}n$.

3. Find $(\partial f/\partial x)_y$, and $(\partial f/\partial y)_x$ for each of the following functions, where a, b, and c are constants.

(a) $f = axy \ln(y)$,
(b) $f = c \sin\left(x^2 y\right)$.

4. Find $(\partial f/\partial x)_y$, and $(\partial f/\partial y)_x$ for each of the following functions, where a, b, and c are constants.

(a) $f = (x+y)/(c+x)$,
(b) $f = (ax+by)^{-2}$.

5. Find $(\partial f/\partial x)_y$, and $(\partial f/\partial y)_x$ for each of the following functions, where a, b, and c are constants.

(a) $f = a\cos^2(bxy)$,
(b) $f = a \exp\left(-b(x^2+y^2)\right)$.

6. Find $(\partial^2 f/\partial x^2)_y$, $(\partial^2 f/\partial x \partial y)$, $(\partial^2 f/\partial y \partial x)$, and $\left(\partial^2 f/\partial y^2\right)$, for each of the following functions, where a, b, and c are constants.

(a) $f = (x+y)^{-2}$,
(b) $f = \cos\left(xy\right)$.

7. Find $(\partial^2 f/\partial x^2)_y$, $(\partial^2 f/\partial x \partial y)$, $(\partial^2 f/\partial y \partial x)$, and $\left(\partial^2 f/\partial y^2\right)$, for each of the following functions, where a, b, and c are constants.

$$f = e^{(ax^2+by^2)},$$
$$f = \ln\left(bx^2 + cy^2\right).$$

8. Find $(\partial^2 f/\partial x^2)_y$, $(\partial^2 f/\partial x \partial y)$, $(\partial^2 f/\partial y \partial x)$, and $\left(\partial^2 f/\partial y^2\right)$, for each of the following functions, where a, b, and c are constants

(a) $f = (x^2 + y^2)^{-1}$,
(b) $f = \sin(xy)$.

9. Test each of the following differentials for exactness.

(a) $\mathrm{d}u = \sec^2(xy)\mathrm{d}x + \tan(xy)\mathrm{d}y$,
(b) $\mathrm{d}u = y\sin\left(xy\right)\mathrm{d}x + x\sin\left(xy\right)\mathrm{d}y$.

10. Test each of the following differentials for exactness.

(a) $\mathrm{d}u = \frac{y}{1+x^2}\mathrm{d}x - \tan^{-1}(x)\mathrm{d}y$,
(b) $\mathrm{d}u = (x^2 + 2x + 1)\mathrm{d}x + (y^2 + 5y + 4)\mathrm{d}y$.

11. Test each of the following differentials for exactness.

(a) $\mathrm{d}u = xy\,\mathrm{d}x + xy\,\mathrm{d}y$,
(b) $\mathrm{d}u = y\,e^{axy}\,\mathrm{d}x + x\,e^{axy}\,\mathrm{d}y$.

12. If $u = RT\ln(aTVn)$ find $\mathrm{d}u$ in terms of $\mathrm{d}T$, $\mathrm{d}V$, and $\mathrm{d}n$, where R and a are constants.

13. Complete the formula

$$\left(\frac{\partial S}{\partial V}\right)_{P,n} = \left(\frac{\partial S}{\partial V}\right)_{T,n} + ?$$

14. Find the location of the minimum in the function

$$f = f(x,y) = x^2 - x - y + y^2$$

considering all real values of x and y. What is the value of the function at the minimum?

15. Find the minimum in the function of the previous problem subject to the constraint $x + y = 2$. Do this by substitution and by the method of undetermined multipliers.

16. Find the location of the maximum in the function

$$f = f(x,y) = x^2 - 6x + 8y + y^2$$

considering the region $0 < x < 2$ and $0 < y < 2$. What is the value of the function at the maximum?

17. Find the maximum in the function of the previous problem subject to the constraint $x + y = 2$. Do this by substitution and by Lagrange's method of undetermined multipliers.

18. Neglecting the attractions of all other celestial bodies, the gravitational potential energy of the earth and the sun is given by

$$\mathcal{V} = -\frac{Gm_\mathrm{s}m_\mathrm{e}}{r},$$

where G is the universal gravitational constant, equal to 6.673×10^{-11} m^3 s^{-2} kg^{-1}, m_s is the mass of the sun, m_e is the mass of the earth, and r is the distance from the center of the sun to the center of the earth. Find an expression for the force on the earth due to the sun using spherical polar coordinates. Compare your result with that using Cartesian coordinates in the example in the chapter.

19. Find an expression for the gradient of the function

$$f(x,y,z) = \cos(xy)\sin(z).$$

20. Find an expression for the divergence of the function

$$\mathbf{F} = \mathbf{i}\sin^2(x) + \mathbf{j}\sin^2(y) + \mathbf{k}\sin^2(z).$$

21. Find an expression for the Laplacian of the function

$$f = r^2\sin(\theta)\cos(\phi).$$

Chapter 9

Integral Calculus with Several Independent Variables

Principal Facts and Ideas

- A line integral is an integral of a differential with several independent variables. It is carried out on a specified path in the space of the independent variables.
- The line integral of an exact differential depends only on the endpoints of the path, but the line integral of an inexact differential depends on the path.
- A multiple integral has as its integrand function a function of several variables, all of which are integrated.

Objectives

After studying this chapter, you should be able to:

- perform a line integral with two independent variables;
- perform a multiple integral;
- change independent variables in a multiple integral.

9.1 LINE INTEGRALS

For a function of a single independent variable x, we wrote in Chapter 7

$$\Delta F = F(x_1) - F(x_0) = \int_{x_0}^{x_1} f(x)\,\mathrm{d}x = \int_{x_0}^{x_1} \mathrm{d}F, \quad (9.1)$$

where

$$f(x) = \frac{\mathrm{d}F}{\mathrm{d}x}. \quad (9.2)$$

We think of the integral of Eq. (9.1) as corresponding to moving along the x axis from x_0 to x_1 as we add up increments.

We now consider the analogous process for a differential with two independent variables:

$$\mathrm{d}F = M(x,y)\,\mathrm{d}x + N(x,y)\mathrm{d}y. \quad (9.3)$$

We need to define a way to integrate from the point $x = x_0, y = y_0$ to the point $x - x_1, y = y_1$. Many different paths in the plane can join the two points. Figure 9.1 depicts one such path and the surface representing the function $F(x,y)$. In order to complete the definition of the integral in Eq. (9.3), we must specify the path from the point (x_0, y_0) to the point (x_1, y_1) along which we add up the infinitesimal increments. We introduce the notation

$$\int_C \mathrm{d}F = \int_C [M(x,y)\,\mathrm{d}x + N(x,y)\mathrm{d}y], \quad (9.4)$$

where the letter C stands for the chosen curve joining the two points. This integral is called a *line integral* or a *path integral*.

Equation (9.4) represents a sum of many infinitesimal contributions, each one given by the appropriate infinitesimal change $\mathrm{d}F$ resulting when x is changed by $\mathrm{d}x$ and y is changed by $\mathrm{d}y$ in such a way that we remain on the chosen curve. A curve in the x–y plane specifies y as a function of x or x as a function of y. For a given curve, we can write

$$y = y(x), \quad (9.5)$$

$$x = x(y). \quad (9.6)$$

In order to calculate a line integral such as that of Eq. (9.4), we replace y in $M(x,y)$ by the function of x given in Eq. (9.5), and we replace x in $N(x,y)$ by the function of y given in Eq. (9.6). With this replacement, M is a function of

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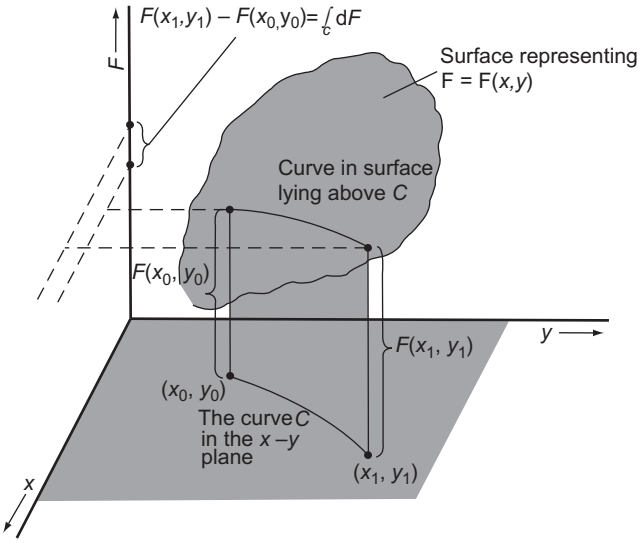

FIGURE 9.1 Diagram illustrating the line integral of an exact differential.

x only, and N is a function of y only, and each term becomes an ordinary one-variable integral:

$$\int_C \mathrm{d}F = \int_{x_0}^{x_1} M\,[x, y(x)]\mathrm{d}x + \int_{y_0}^{y_1} N\,[y, x(y)]\mathrm{d}y. \quad (9.7)$$

In these integrals, specification of the curve C determines not only what the beginning point (x_0, y_0) and the final point (x_1, y_1) are, but also what the functions are that replace y in the dx integral and x in the dy integral.

Example 9.1. Find the value of the line integral

$$\int_C \mathrm{d}F = \int_c [(2x + 3y)\mathrm{d}x + (3x + 4y)\mathrm{d}y],$$

where c is the straight-line segment given by $y = 2x + 3$ from (0,3) to (2,7).

In the first term, y must be replaced by $2x + 3$, and in the second term x must be replaced by $(1/2)(y - 3)$,

$$\begin{aligned}\int_c \mathrm{d}F &= \int_0^2 [2x + 3(2x + 3)]\mathrm{d}x \\ &\quad + \int_3^7 \left[\frac{3}{2}(y - 3) + 4y\right]\mathrm{d}y \\ &= \left(\frac{8x^2}{2} + 9x\right)\Bigg|_0^2 + \left(\frac{(11/2)\,y^2}{2} - \frac{9}{2}y\right)\Bigg|_3^7 \\ &= 126.\end{aligned}$$

Exercise 9.1. Show that the differential in the preceding example is exact.

9.1.1 Line Integrals of Exact Differentials

There is an important theorem, which we now state without proof: *If dF is an exact differential, then the line integral $\int_C dF$ depends only on the initial and final points and not on the choice of curve joining these points. Further, the line integral equals the value of the function F at the final point minus the value of the function at the beginning point.* We say that the line integral of an exact differential is path-independent.

For example, if (x_0, y_0) is the initial point of the line integration and (x_1, y_1) is the final point of the line integration, then

$$\begin{aligned}\int_C \mathrm{d}F &= \int_C \left[\left(\frac{\partial F}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial F}{\partial y}\right)_x \mathrm{d}y\right] \\ &= F\left(x_1, y_1\right) - F\left(x_0, y_0\right) \quad (\mathrm{d}F \text{ exact}). \quad (9.8)\end{aligned}$$

We have written M and N as the partial derivatives which they must be equal to in order for dF to be exact. If du is an inexact differential, there is no such thing as a function u, and the line integral will depend not only on the beginning and ending points, but also on the curve of integration joining these points.

Example 9.2. Show that the line integral of the previous example has the same value as the line integral of the same differential on the rectangular path from (0,3) to (2,3) and then to (2,7).

The path of this integration is not a single curve but two line segments, so we carry out the integration separately for each segment. This is actually a simplification, because on the first line segment, y is constant, so d$y = 0$ and the dy integral vanishes. On the second line segment, x is constant, so d$x = 0$ and the dx integral vanishes. Therefore,

$$\int_c \mathrm{d}F = \int_0^2 (2x + 9)\mathrm{d}x + \int_3^7 (6 + 4y)\mathrm{d}y.$$

This follows from the fact that $y = 3$ on the first line segment, and from the fact that $x = 2$ on the second line segment. Performing the integration yields

$$\int_c \mathrm{d}F = \left(\frac{2x^2}{2} + 9x\right)\Bigg|_0^2 + \left(6y + \frac{4y^2}{2}\right)\Bigg|_3^7 = 126.$$

Exercise 9.2. **(a)** Show that the following differential is exact:

$$\mathrm{d}z = (ye^{xy})\mathrm{d}x + (xe^{ey})\mathrm{d}y.$$

(b) Calculate the line integral $\int_c \mathrm{d}z$ on the line segment from (0,0) to (2,2). On this line segment, $y = x$ and $x = y$.

(c) Calculate the line integral $\int_c \mathrm{d}z$ on the path going from (0,0) to (0,2) and then to (2,2) (a rectangular path).

9.1.2 Line Integrals of Inexact Differentials

If a differential is not exact, two line integrals on curves beginning and ending at the same points will not necessarily yield the same result.

Example 9.3. Show that the differential

$$du = dx + x\,dy$$

is inexact and carry out the line integral from (0,0) to (2,2) by two different paths: path 1: the straight-line segment from (0,0) to (2,2); and path 2: the rectangular path from (0,0) to (2,0) and then to (2,2).

Test for exactness:

$$\left[\frac{\partial}{\partial y}(1)\right]_x = 0,$$
$$\left[\frac{\partial}{\partial x}(x)\right]_y = 1 \neq 0.$$

The differential is not exact.

Path 1:

$$\int_{C_1} du = \int_{C_1} dx + \int_{C_1} x\,dy = \int_0^2 dx + \int_0^2 y\,dy,$$

where we obtained the second integral by using the fact that $y = x$ on the straight-line segment of path 1,

$$\int_{C_1} du = x^2\Big|_0^2 + \frac{y^2}{2}\Big|_0^2 = 4.$$

Path 2:

$$\int_{C_2} du = \int_{C_2} dx + \int_{C_2} x\,dy = \int_0^2 dx + \int_0^2 2\,dy$$
$$= x|_0^2 + 2y|_0^2 = 2 + 4 = 6.$$

The two line integrals have the same beginning point and the same ending point, but are not equal to each other, because the differential is not an exact differential.

Exercise 9.3. Carry out the line integral of $du = dx + x\,dy$ from (0,0) to (x_1, y_1):

(a) On the rectangular path from (0,0) to $(0, y_1)$ and then to (x_1, y_1).
(b) On the rectangular path from (0,0) to $(x_1, 0)$ and then to (x_1, y_1).

9.1.3 Line Integrals with Three Integration Variables

There are also line integrals of functions of three independent variables. If

$$du = M(x,y,z)dx + N(x,y,z)dy + P(x,y,z)dz, \quad (9.9)$$

then the line integral of the differential du is

$$\int_c du = \int_c [M(x,y,z)\,dx + N(x,y,z)dy + P(x,y,z)dz], \quad (9.10)$$

where C specifies a curve that gives y and z as functions of x, or x and y as functions of z, or x and z as functions of y. The curve C represents a path in three-dimensional space. In the first term of the integral, y must be replaced by the appropriate function of x and z must be replaced by the appropriate function of dx corresponding to the chosen path. Analogous replacements must be made in the other two terms. If the beginning point of the curve C is (x_0, y_0, z_0) and the ending point is (x_1, y_1, z_1), the line integral is

$$\int_c du = \int_{x_0}^{x_1} M[x, y(x), z(x)]dx + \int_{y_0}^{y_1} N\left[x(y), y, z(y)\right]dy + \int_{y_0}^{y_1} P[x(z), y(z), z]dy. \quad (9.11)$$

If du is an exact differential, then u is a function, and the path integral depends only on the beginning and ending points:

$$\boxed{\int_c du = \Delta u = u(x_1,y_1,z_1) - u(x_0,y_0,z_0) \quad \text{(if } du \text{ is an exact differential)}}, \quad (9.12)$$

where we use the common notation Δu for u(final) − u(initial).

Example 9.4. Consider the differential

$$du = yz\,dx + xz\,dy + xy\,dz. \quad (9.13)$$

Determine whether the differential is exact and evaluate the line integral

$$\int_c du = \int_c (M\,dx + N\,dy + P\,dz) = \int_c (yz\,dx + xz\,dy + xy\,dz) \quad (9.14)$$

on the path from (0,0,0) to (3,3,3) corresponding to $x = y = z$.

Test for exactness:

$$\left(\frac{\partial M}{\partial y}\right)_{x,z} = z = \left(\frac{\partial N}{\partial x}\right)_{y,z}, \quad (9.15)$$
$$\left(\frac{\partial N}{\partial z}\right)_{x,y} = x = \left(\frac{\partial P}{\partial y}\right)_{x,z}, \quad (9.16)$$
$$\left(\frac{\partial M}{\partial z}\right)_{x,y} = y = \left(\frac{\partial P}{\partial x}\right)_{y,z}. \quad (9.17)$$

The differential is exact. In the integrands, we replace x by either y or z, y by either x or z, and z by either x or y in order to get an ordinary integral in each term. We can now specify the limits of each integration.

The result is

$$\int_c \mathrm{d}u = \int_0^3 x^2\,\mathrm{d}x + \int_0^3 y^2\,\mathrm{d}y + \int_0^3 z^2\,\mathrm{d}z = \frac{1}{3}3^3 + \frac{1}{3}3^3 + \frac{1}{3}3^3 = 27. \tag{9.18}$$

The function possessing this differential is $u = xyz$ and the line integral is equal to the value of the function evaluated at the endpoint of the integration minus the value at the starting point:

$$\int_c (yz\,\mathrm{d}x + xz\,\mathrm{d}y + xy\,\mathrm{d}z) = u(3,3,3) - u(0,0,0) = 27 - 0 = 27. \tag{9.19}$$

In this example, it was much easier to evaluate the function at the ends of the interval than to carry out the integration. In thermodynamics, this is not usually the case.

Exercise 9.4. Carry out the line integral of the previous example, $\mathrm{d}u = yz\,\mathrm{d}x + xz\,\mathrm{d}y + xy\,\mathrm{d}z$, on the path from (0,0,0) to (3,0,0) and then from (3,0,0) to (3,3,0) and then from (3,3,0) to (3,3,3).

9.1.4 Line Integrals in Thermodynamics

In thermodynamics, the *equilibrium state* of a system is represented by a point in a space whose axes represent the variables specifying the state of the system. A line integral in such a space represents a *reversible process*. In a reversible process, the direction of the process can be changed by an infinitesimal change in the system's surroundings, and the system remains at equilibrium during the process. A reversible process must proceed infinitely slowly, and is not possible in the real world, but can be approximated in some cases. A *cyclic process* is one that begins and ends at the same state of the system. A line integral that begins and ends at the same point is denoted by the symbol $\oint \mathrm{d}u$. Since the beginning and final points are the same, such an integral must vanish if $\mathrm{d}u$ is an exact differential:

$$\boxed{\oint \mathrm{d}u = 0 \quad \text{(if } \mathrm{d}u \text{ is exact)}}. \tag{9.20}$$

If $\mathrm{d}u$ is inexact, a line integral that begins and ends at the same point will not necessarily be equal to zero. In thermodynamics, the principal inexact differentials are those for an infinitesimal amount of work done and the amount of heat transferred in a reversible process. The differential representing the amount of work done on a fluid system in a reversible process is

$$\mathrm{d}w_{\mathrm{rev}} = -P\,\mathrm{d}V. \tag{9.21}$$

This is not an exact differential. We see in the next example that its cyclic integral does not necessarily vanish. Since $\mathrm{d}w_{\mathrm{rev}}$ is not exact, we write

$$\int_c \mathrm{d}w_{\mathrm{rev}} = w_{\mathrm{rev}}, \tag{9.22}$$

rather than using the Δw notation.

Example 9.5. Carry out the cyclic line integral of $\mathrm{d}w_{\mathrm{rev}}$ for 1.000 mol of an ideal gas, using the following reversible cycle: (1) Starting with T = 500.0 K and V = 20.0 l, the system is expanded at constant temperature to a volume of 40.0 l. (2) The system is cooled at constant volume to 300.0 K. (3) The system is then compressed to a volume of 20.0 l at a constant temperature of 300.0 K. (4) It is heated at constant volume to 600.0 K.

We carry out the integration for each step separately. For Step 1, $\mathrm{d}T = 0$, so that

$$\begin{aligned} w_{\mathrm{rev},1} &= \int_c \mathrm{d}w_{\mathrm{rev}} = -\int_c P\,\mathrm{d}V = -\int_c \frac{nRT}{V}\,\mathrm{d}V \\ &= -nRT\int_{V_1}^{V_2} \frac{1}{V}\mathrm{d}V \\ &= -nRT\ln\left(\frac{V_2}{V_1}\right) = -(1.000\ \mathrm{mol}) \\ &\quad \times (8.3145\ \mathrm{J\ K\ mol^{-1}})(500.0\ \mathrm{K})\ln\left(\frac{40.0\ \mathrm{l}}{20.0\ \mathrm{l}}\right) \\ &= -2882\ J. \end{aligned}$$

Note that since the volumes occur as a ratio, we do not have to convert to the SI unit of volume, m^3. For Step 2, $\mathrm{d}V = 0$

$$w_{\mathrm{rev},2} = \int_c \mathrm{d}w_{\mathrm{rev}} = 0.$$

For any constant-volume process, the line integral of $\mathrm{d}w_{\mathrm{rev}}$ vanishes. For Step 3, $\mathrm{d}T = 0$, so the calculation is similar to that for Step 1:

$$\begin{aligned} w_{\mathrm{rev},3} &= \int_c \mathrm{d}w_{\mathrm{rev}} = -\int_c P\,\mathrm{d}V = -\int_c \frac{nRT}{V}\mathrm{d}V \\ &= -nRT\int_{V_1}^{V_2} \frac{1}{V}\mathrm{d}V \\ &= -nRT\ln\left(\frac{V_2}{V_1}\right) = -(1.000\ \mathrm{mol}) \\ &\quad \times (8.3145\ \mathrm{J\ K\ mol^{-1}})(300.0\ \mathrm{K})\ln\left(\frac{20.0\ \mathrm{l}}{40.0\ \mathrm{l}}\right) \\ &= 1729\ \mathrm{J}. \end{aligned}$$

Step 4 is similar to Step 2, contributing zero. For the entire cycle

$$\boxed{w_{\mathrm{rev}} = \oint \mathrm{d}w_{\mathrm{rev}} = -2882\ \mathrm{J} + 1729\ \mathrm{J} = -1153\ \mathrm{J}}.$$

The cyclic integral does not vanish because $\mathrm{d}w_{\mathrm{rev}}$ is an inexact differential.

Exercise 9.5. A two-phase system contains both liquid and gaseous water, so its equilibrium pressure is determined by the temperature. Calculate the cyclic integral of $\mathrm{d}w_{\mathrm{rev}}$ for the following process: The volume of the system is changed from 10.00 l to 20.00 l at a constant temperature of 25.00° C, at which the pressure is 24.756 torr. The system is then heated to a temperature of 100.0° C at a constant volume of 20.00 l. The system is then compressed to a volume of 10.00 l at a temperature of 100.0° C, at which the pressure is 760.0 torr. The system is then cooled from 100.0° C to a temperature of 25.00° C at a constant volume of 10.00 l. Remember to use consistent units.

An infinitesimal amount of heat $\mathrm{d}q$ transferred in a reversible process is also not an exact differential. Just as with $\mathrm{d}w$ we do not use the Δ notation, and write

$$\int_C \mathrm{d}q = q. \tag{9.23}$$

The first law of thermodynamics implies that $\mathrm{d}U$ is an exact differential, where

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w. \tag{9.24}$$

The function possessing $\mathrm{d}U$ as its differential is called the *thermodynamic energy*. Since $\mathrm{d}U$ is exact, U is a state function, and we can write

$$\Delta U = q + w,$$

even though q and w are not functions. For a cyclic process such as that of the previous example

$$\Delta U = q + w = 0 \quad \text{(cyclic process)}, \tag{9.25}$$

$$q = -w \quad \text{(cyclic process)}. \tag{9.26}$$

In the process of the previous example, 1153 J of heat must have been transferred to the system.

If an infinitesimal amount of heat, $\mathrm{d}q_{\mathrm{rev}}$, is transferred to a system at constant pressure and if no chemical reaction or phase change occurs, we can write

$$\mathrm{d}q_{\mathrm{rev}} = C_P\,\mathrm{d}T, \tag{9.27}$$

where C_P is called the *heat capacity at constant pressure* and where $\mathrm{d}T$ is an infinitesimal change in the temperature. A process in which no heat is transferred is called an *adiabatic process*.

$$\mathrm{d}q_{\mathrm{ad}} = 0 \quad \text{(adiabatic process)}.$$

For an adiabatic process

$$\mathrm{d}U_{\mathrm{ad}} = \mathrm{d}w_{\mathrm{ad}}. \tag{9.28}$$

Exercise 9.6. The thermodynamic energy of a monatomic ideal gas is temperature-independent, so that $\mathrm{d}U = 0$ in an isothermal process (one in which the temperature does not change). Evaluate w_{rev} and q_{rev} for the isothermal reversible expansion of 1.000 mol of a monatomic ideal gas from a volume of 15.50 l to a volume of 24.40 l at a constant temperature of 298.15 K.

9.2 MULTIPLE INTEGRALS

With more than one independent variable, there is another type of integral in addition to line integrals. While a line integral can be thought of as adding up infinitesimal contributions represented as a differential form, a *multiple integral* can be thought of as adding up contributions given by an integrand function times an infinitesimal element of area or volume.

9.2.1 Double Integrals

A *double integral* involves an integrand depending on two independent variables. If the limits of integration are constants, it is written in the form

$$I = \int_{a_1}^{a_2} \int_{b_1}^{b_2} f(x,y)\mathrm{d}y\,\mathrm{d}x, \tag{9.29}$$

where $f(x,y)$ is the integrand function, b_1 and b_2 are the limits of the y integration and a_1 and a_2 are the limits of the x integration. The product $\mathrm{d}y\,\mathrm{d}x$ represents an infinitesimal element of area in the x–y plane. We first carry out the inner integration (the one for which the differential and limits are written closest to the integrand function). During this integration, the other independent variable is treated as a constant. The result of the first integration is the integrand for the remaining integration. The limits b_1 and b_2 can depend on x, but the limits a_1 and a_2 must be constants.

Example 9.6. Evaluate the double integral

$$I = \int_0^a \int_0^b (x^2 + 4xy)\mathrm{d}y\,\mathrm{d}x.$$

The integration over y is carried out, treating x as a constant:

$$\int_0^b (x^2 + 4xy)\mathrm{d}y = \left(x^2 y + \frac{4xy^2}{2}\right)\Bigg|_0^b = bx^2 + 2b^2 x.$$

This result is the integrand for the second integration, so that

$$I = \int_0^a (bx^2 + 2b^2 x)\mathrm{d}x = \left(\frac{bx^3}{3} + \frac{2b^2x^2}{2}\right)\Bigg|_0^a$$

$$= \frac{ba^3}{3} + b^2a^2.$$

In the next example, we have a case in which the limits of the first integration depend on the variable in the second integration.

Example 9.7. Evaluate the double integral

$$\int_0^a \int_0^{3x} (x^2 + 2xy + y^2)\mathrm{d}y\,\mathrm{d}x.$$

The result of the inside integration is

$$\int_0^{3x} \left(x^2 + 2xy + y^2\right)\mathrm{d}y = \left(x^2 y + \frac{2xy^2}{2} + \frac{y^3}{3}\right)\Bigg|_0^{3x} = 3x^3 + 9x^3 + 9x^3 = 21x^3.$$

The x integration gives

$$\int_0^a 21x^3\,\mathrm{d}x = \frac{21x^4}{4}\Bigg|_0^a = \frac{21a^4}{4}.$$

Exercise 9.7. Evaluate the double integral

$$\int_2^4 \int_0^{\pi} x \sin^2(y)\mathrm{d}y\,\mathrm{d}x.$$

9.2.2 The Double Integral Representing a Volume

In Section 7.2 we saw that a definite integral with one independent variable is equal to an area in a graph. A double integral is equal to a volume in an analogous way. This is illustrated in Figure 9.2, which is drawn to correspond to Example 9.8. In the x–y plane, we have an infinitesimal element of area $\mathrm{d}x\,\mathrm{d}y$, drawn in the figure as though it were finite in size. The vertical distance from the x–y plane to the surface representing the integrand function f is the value of the integrand function, so that the volume of the small box lying between the element of area and the surface is equal to $f(x,y)\,\mathrm{d}x\,\mathrm{d}y$.

The double integral is the sum of the volume of all such infinitesimal boxes, and thus equals the volume of the solid bounded by the x–y plane, the surface representing the integrand function, and surfaces representing the limits of integration. If the integrand function is negative in part of the region of integration, we must take the volume above the x–y plane as positive and the volume below the plane as negative.

Example 9.8. Calculate the volume of the solid shown in Figure 9.2. The bottom of the solid is the x–y plane. The flat vertical surface corresponds to $y = 0$, the curved vertical surface corresponds to $y = x^2 - 4$, and the top of the solid corresponds to $f(x,y) = 2 - y$.

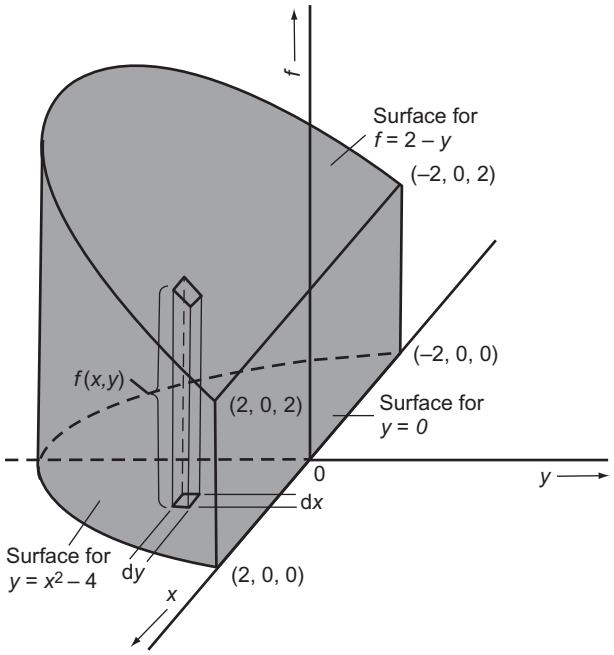

FIGURE 9.2 The diagram for Example 9.8.

We carry out a double integral with $f(x,y) = 2 - y$ as the integrand:

$$V = \int_{-2}^{2} \int_{x^2-4}^{0} (2 - y)\mathrm{d}y\,\mathrm{d}x.$$

The inside integral is

$$\begin{aligned}\int_{x^2-4}^{0} (2 - y)\mathrm{d}y &= \left(2y - \frac{y^2}{2}\right)\Bigg|_{x^2-4}^{0} \\ &= 0 - \left[2(x^2 - 4) - \left(\frac{(x^2-4)^2}{2}\right)\right] \\ &= -2x^2 + 8 + \frac{x^4 - 8x^2 + 16}{2} \\ &= \frac{x^4}{2} - 6x^2 + 16.\end{aligned}$$

The limit of the y integration is a function of x. This integration must be placed next to the integrand and done first. We now have

$$\begin{aligned}V &= \int_{-2}^{2} \left(\frac{x^4}{2} - 6x^2 - 16\right)\mathrm{d}x \\ &= \left(\frac{x^5}{10} - 2x^3 - 16x\right)\Bigg|_{-2}^{2} = 38.4.\end{aligned}$$

Exercise 9.8. Find the volume of the solid object shown in Figure 9.3. The top of the object corresponds to

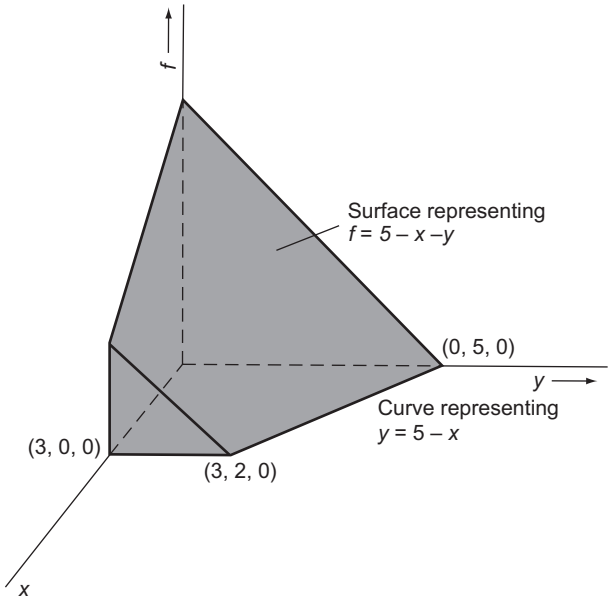

FIGURE 9.3 The diagram for Exercise 9.8.

$f = 5.00 - x - y$, the bottom of the object is the x–y plane, the trapezoidal face is the x–f plane, and the large triangular face is the y–f plane. The small triangular face corresponds to $x = 3.00$.

9.2.3 Triple Integrals

In quantum mechanics, the square of a wave function is the probability density (probability per unit volume) for finding a particle or particles. A multiple integral with three independent variables (*a triple integral*) represents the probability of finding a particle in the three-dimension region of the integration. For example, if the wave function ψ depends on x, y, and z, the triple integral

$$I = \int_{a_1}^{a_2} \int_{b_1}^{b_2} \int_{c_1}^{c_2} \psi^2(x,y,z)\mathrm{d}z\,\mathrm{d}y\,\mathrm{d}x \tag{9.30}$$

represents the probability of finding the particle in the rectangular box given by $a_1 \le x \le a_2, b_1 \le y \le b_2, c_1 \le z \le c_2$. To evaluate the integral, we first integrate z from c_1 to c_2 and take the result as the integrand for the double integral over y and x. Then we integrate y from b_1 to b_2, and take the result as the integrand for the integral over x from a_1 to a_2. The limits c_1 and c_2 could be replaced by a function of y and x, and the limits b_1 and b_2 could be replaced by a function of x. The limits of the last integration, a_1 and a_2, must be constants. If the limits are all constants, and if the integrand function can be factored, the entire integral can be factored, as in the following example.

Example 9.9. Find the triple integral

$$I = A^2 \int_0^a \int_0^b \int_0^c \sin^2\left(\frac{n\pi x}{a}\right) \times \sin^2\left(\frac{m\pi y}{b}\right) \sin^2\left(\frac{k\pi z}{c}\right) \mathrm{d}z\,\mathrm{d}y\,\mathrm{d}x.$$

This integral is equal to the total probability for finding a particle in a three-dimensional box, given that the wave function corresponds to the quantum numbers n, m, and k. It is customary to choose the value of the constant A so that the total probability equals unity, in which case the wave function is said to be normalized.

The integrand function is a product of three factors, each of which depends on only one variable, and the limits of integration are constants. The entire integral can be factored:

$$I = A^2 \left[\int_0^a \sin^2\left(\frac{n\pi x}{a}\right)\mathrm{d}x\right]\left[\int_0^b \sin^2\left(\frac{m\pi y}{b}\right)\mathrm{d}y\right] \left[\int_0^c \sin^2\left(\frac{k\pi z}{c}\right)\mathrm{d}z\right].$$

We first carry out the z integration, using the substitution $u = k\pi z/c$,

$$\int_0^c \sin^2\left(\frac{k\pi z}{c}\right)\mathrm{d}z = \frac{c}{k\pi}\int_0^{k\pi} \sin^2(u)\mathrm{d}u.$$

The integrand is a periodic function with period π, so that the integral from 0 to $k\pi$ is just k times the integral from 0 to π, which is given as Eq. (8) of Appendix F, with m = n = 1

$$\int_0^c \sin^2\left(\frac{k\pi z}{c}\right)\mathrm{d}z = \frac{c}{k\pi}k\frac{\pi}{2} = \frac{c}{2}.$$

The other integrals are similar, except for having a or b instead of c, so that

$$I = A^2\frac{abc}{8}.$$

If we wish to assign a value to the constant A so that the wave function is normalized, we have

$$A = \sqrt{\frac{8}{abc}}.$$

Exercise 9.9. Find the value of the constant A such that the following integral equals unity:

$$A\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-x^2-y^2}\mathrm{d}y\,\mathrm{d}x.$$

9.2.4 Changing Variables in Multiple Integrals

Sometimes it is convenient to compute a multiple integral using polar coordinates or spherical polar coordinates instead of Cartesian coordinates.

Double Integrals

Figure 9.4 shows how a double integral is carried out in polar coordinates. We consider the integral to be a sum of contributions, each one of which is an infinitesimal area times the value of the integrand function at that area. One dimension of the element of area is $\mathrm{d}\rho$ and the other dimension is $\rho\,\mathrm{d}\phi$, from the fact that an arc length is the radius of the circle times the angle subtended by the arc, measured in radians. The element of area is $\rho\,\mathrm{d}\phi\,\mathrm{d}\rho$. If the element of area were finite, it would not be rectangular, but this formula is valid for an infinitesimal element of area.

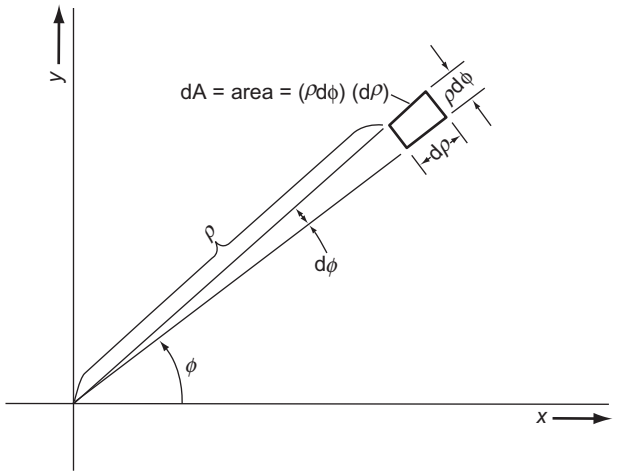

FIGURE 9.4 An infinitesimal element of area in plane polar coordinates.

Example 9.10. In Cartesian coordinates, the wave function for the ground state of a two-dimensional harmonic oscillator is

$$\psi = B\exp[-a(x^2+y^2)],$$

where B and a are constants. Transform this to plane polar coordinates and find the value of B such that the integral of ψ^2 over the entire x–y plane is equal to unity.

In polar coordinates,

$$\psi = Be^{-a\rho^2}.$$

We require that

$$B^2\int_0^\infty\int_0^{2\pi} e^{-2a\rho^2}\,\rho\,\mathrm{d}\phi\,\mathrm{d}\rho = 1.$$

The integral can be factored,

$$B^2\int_0^\infty e^{-2a\rho^2}\,\rho\,\mathrm{d}\rho\int_0^{2\pi}\mathrm{d}\phi = 2\pi B^2\int_0^\infty e^{-2a\rho^2}\,\rho\,\mathrm{d}\rho.$$

The ρ integral is done by the method of substitution, letting $u = 2a\rho^2$ and $\mathrm{d}u = 4a\rho\,\mathrm{d}\rho$. We obtain

$$1 = 2\pi B^2\left(\frac{1}{4a}\right)\int_0^\infty e^{-u}\,\mathrm{d}u = \frac{B^2\pi}{2a},$$

$$B = \sqrt{\frac{2a}{\pi}}.$$

Exercise 9.10. Use a double integral to find the volume of a cone of height h and radius a at the base. If the cone is standing with its point upward and with its base centered at the origin, the equation giving the height of the surface of the cone as a function of ρ is

$$f = h\left(1-\frac{\rho}{a}\right).$$

In transforming from Cartesian to plane polar coordinates, the factor ρ that is used with the product of the differentials $\mathrm{d}\phi\,\mathrm{d}\rho$ is an example of a *Jacobian*. The symbol $\partial(x,y)/\partial(\rho,\phi)$ is used for this Jacobian:

$$\begin{aligned}\iint f(x,y)\mathrm{d}x\,\mathrm{d}y &= \iint f\left(\rho,\phi\right)\,\mathrm{d}\phi\,\mathrm{d}\rho\\ &= \iint f\left(\rho,\phi\right)\frac{\partial(x,y)}{\partial(\rho,\phi)}\mathrm{d}\rho\,\mathrm{d}\phi.\end{aligned} \tag{9.31}$$

We will not discuss the mathematical theory, but this Jacobian is given by the following determinant (determinants are discussed in Chapter 13):

$$\frac{\partial(x,y)}{\partial(\rho,\phi)} = \begin{vmatrix}\partial x/\partial\rho & \partial x/\partial\phi\\ \partial y/\partial\rho & \partial y/\partial\phi\end{vmatrix}. \tag{9.32}$$

From Chapter 13 we have the formula for a 2 by 2 determinant:

$$\begin{aligned}\begin{vmatrix}\partial x/\partial\rho & \partial x/\partial\phi\\ \partial y/\partial\rho & \partial y/\partial\phi\end{vmatrix} &= \begin{vmatrix}\cos(\phi) & -\rho\sin(\phi)\\ \cos(\phi) & \rho\cos(\phi)\end{vmatrix}\\ &= \rho\cos^2(\phi)+\rho\sin^2(\phi) = \rho,\end{aligned} \tag{9.33}$$

where we have also used the identity in Eq. (7) of Appendix B. This equation gives us the same result that we had before,

$$\mathrm{d}A = \text{element of area} = \rho\,\mathrm{d}\phi\,\mathrm{d}\rho. \tag{9.34}$$

Triple Integrals

Changing variables in three dimensions requires the appropriate Jacobian. Figure 9.5 depicts the element of volume in spherical polar coordinates. The length of the little "box" in the r direction is $\mathrm{d}r$, the length in the θ direction $r\,\mathrm{d}\theta$, and the length in the ϕ direction is $r\sin(\theta)\,\mathrm{d}\phi$ so that the Jacobian is equal to $r^2\sin(\theta)$.

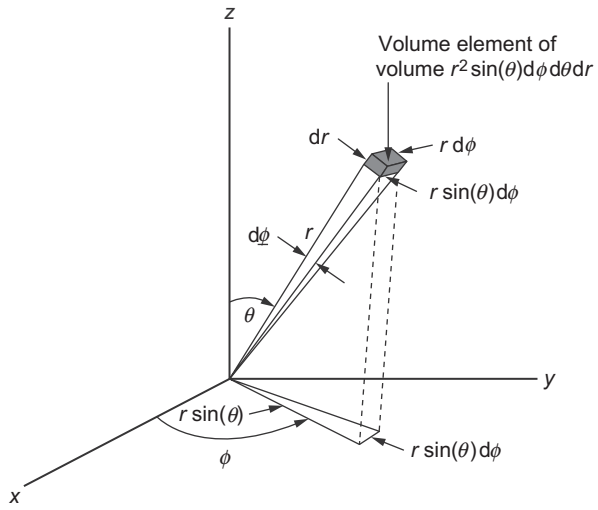

FIGURE 9.5 An infinitesimal element of volume in spherical polar coordinates.

In addition to inspection of the lengths in three dimensions, we can determine the Jacobian using a determinant, as with two dimensions. If u, v, and w are some set of coordinates such that

$$\begin{aligned} x &= x(u,v,w), \\ y &= y(u,v,w), \\ z &= z(u,v,w), \end{aligned}$$

then the Jacobian for the transformation of a multiple integral from Cartesian coordinates to the coordinates u, v, and w is given by the determinant

$$\boxed{\frac{\partial(x,y,z)}{\partial(u,v,w)} = \begin{vmatrix} \partial x/\partial u & \partial x/\partial v & \partial x/\partial w \\ \partial y/\partial u & \partial y/\partial v & \partial y/\partial w \\ \partial z/\partial u & \partial z/\partial v & \partial z/\partial w \end{vmatrix}}. \tag{9.35}$$

Example 9.11. Obtain the Jacobian for the transformation from Cartesian coordinates to spherical polar coordinates.

The equations relating the coordinates are Eqs. (3.8)–(3.10)

$$\frac{\partial(x,y,z)}{\partial(r,\theta,\phi)} = \begin{vmatrix} \sin(\theta)\cos(\theta) & r\cos(\theta)\cos(\phi) & -r\sin(\theta)\sin(\phi) \\ \sin(\theta)\sin(\phi) & r\cos(\theta)\sin(\phi) & r\sin(\theta)\cos(\phi) \\ \cos(\phi) & -r\sin(\theta) & 0 \end{vmatrix}.$$

From the rule for expansion of a 3 by 3 determinant (see Chapter 13)

$$\begin{aligned} \frac{\partial(x,y,z)}{\partial(r,\theta,\phi)} &= \cos(\theta)\left[r^2\cos(\theta)\sin(\theta)\cos^2(\phi) + r^2\sin(\theta)\cos(\theta)\sin^2(\theta)\right] \\ &\quad + r\sin(\theta)\left[r\sin^2(\theta)\cos^2(\phi) + r^2\sin^2(\theta)(\phi)\right] \\ &= r\sin(\theta)\cos^2(\theta) + r^2\sin^3(\theta) = r^2\sin(\theta), \end{aligned}$$

where we have used Eq. (7) of Appendix B several times. The result is the same as our result from geometrical analysis, which of course was easier.

Exercise 9.11. Find the Jacobian for the transformation from Cartesian to cylindrical polar coordinates.

A triple integral in Cartesian coordinates is transformed into a triple integral in spherical polar coordinates by

$$\begin{aligned} &\iiint f(x,y,z)\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \\ &\quad = \iiint f(r,\theta,\phi)r^2\sin(\theta)\,\mathrm{d}\phi\,\mathrm{d}\theta\,\mathrm{d}r. \end{aligned} \tag{9.36}$$

To complete the transformation, the limits on r, θ, and ϕ must be found so that they correspond to the limits on x, y, and z. Sometimes the purpose of transforming to spherical polar coordinates is to avoid the task of finding the limits in Cartesian coordinates when they can be expressed easily in spherical polar coordinates. For example, if the integration is over the interior of a sphere of radius a centered at the origin, ϕ ranges from 0 to 2π, θ ranges from 0 to π and r ranges from 0 to a. If all of space is to be integrated over, ϕ ranges from 0 to 2π, θ ranges from 0 to π, and r ranges from 0 to ∞.

Example 9.12. Evaluate the integral

$$I = \int_0^{3.00}\int_0^{\pi}\int_0^{2\pi} r\cos^2(\phi)r^2\sin(\theta)\,\mathrm{d}\phi\,\mathrm{d}\theta\,\mathrm{d}r.$$

The integral can be factored:

$$\begin{aligned} I &= \int_0^{2\pi}\cos^2(\phi)\,\mathrm{d}\phi\int_0^{\pi}\sin(\theta)\,\mathrm{d}\theta\int_0^{3.00} r^3\,\mathrm{d}r, \\ &\int_0^{2\pi}\cos^2(\phi)\,\mathrm{d}\phi = \left[\frac{\phi}{2} + \frac{\sin(2\phi)}{4}\right]_0^{2\pi} = \pi, \\ &\int_0^{\pi}\sin(\theta)\mathrm{d}\theta = -\cos(\theta)|_0^{\pi} = -(-1) + 1 = 2, \\ &\int_0^{3.00} r^4\,\mathrm{d}r = \frac{1}{4}(3.00)^4 = 20.25, \\ &I = \pi \times 2 \times 20.25 = 127.23. \end{aligned}$$

Exercise 9.12. Evaluate the triple integral in cylindrical polar coordinates:

$$I = \int_0^{3.00} \int_0^{4.00} \int_0^{2\pi} z\rho^3 \cos^2(\phi)\, \mathrm{d}\phi\, \mathrm{d}\rho\, \mathrm{d}z.$$

PROBLEMS

1. Perform the line integral

$$\int_c \mathrm{d}u = \int_c (x^2 y\, \mathrm{d}x + xy^2\, \mathrm{d}y).$$

(a) On the line segment from (0,0) to (2,2).
(b) On the path from (0,0) to (2,0) and then from (2,0) to (2,2).

2. Perform the line integral

$$\int_c \mathrm{d}u = \int_c (y\, \mathrm{d}x + x\, \mathrm{d}y)$$

on the curve represented by

$$y = x^2$$

from (0,0) to (2,4).

3. Perform the line integral

$$\int_c \mathrm{d}u = \int_c \left(\frac{1}{x}\mathrm{d}x + \frac{1}{y}\mathrm{d}y\right)$$

on the curve represented by

$$y = x$$

from (1,1) to (2,2).

4. Find the function whose differential is

$$\mathrm{d}f = \cos(x)\cos(y)\mathrm{d}x - \sin(x)\sin(y)\mathrm{d}y$$

and whose value at $x = 0$, $y = 0$ is 0.

5. Find the function $f(x,y)$ whose differential is

$$\mathrm{d}f = (x+y)^{-1}\mathrm{d}x + (x+y)^{-1}\mathrm{d}y$$

and which has the value $f(1,1) = 0$. Do this by performing a line integral on a rectangular path from (1,1) to (x_1, y_1) where $x_1 > 0$ and $y_1 > 0$.

6. Find the function whose exact differential is

$$\begin{aligned}\mathrm{d}f = {} & \cos(x)\sin(y)\sin(z)\mathrm{d}x \\ & + \sin(x)\cos(y)\sin(z)\mathrm{d}y \\ & + \sin(x)\sin(y)\cos(z)\mathrm{d}z\end{aligned}$$

and whose value at (0,0,0) is 0. Find the area of the circle of radius a given by

$$\rho = a$$

by doing the double integral

$$\int_0^a \int_0^{2\pi} 1\, \mathrm{d}\phi\, \mathrm{d}\rho.$$

7. Find the moment of inertia of a uniform disk of radius 0.500 m and a mass per unit area of 25.00 g m^2. The *moment of inertia* is defined by

$$I = \iint m(\rho)\rho^2\, \mathrm{d}A = \int_r^R \int_0^{2\pi} m(\rho)\rho^2 \rho\, \mathrm{d}\phi\, \mathrm{d}\rho,$$

where $m(\rho)$ is the mass per unit area.

8. A flywheel of radius R has a distribution of mass given by

$$m(\rho) = a\rho + b,$$

where ρ, is the distance from the center, a and b are constants, and $m(\rho)$ is the mass per unit area as a function of ρ. The flywheel has a circular hole in the center with radius r. Find an expression for the *moment of inertia*, defined by $I = \iint m(\rho)\rho^2\, \mathrm{d}A = \int_r^R \int_0^{2\pi} m(\rho)\rho^2 \rho\, \mathrm{d}\phi\, \mathrm{d}\rho$.

9. Find an expression for the moment of inertia of a thin hollow sphere of radius a and a uniform mass per unit area of m. Evaluate your expression if $a = 0.500$ m, $\Delta a = 0.112$ mm, $m = 3515$ kg m^{-3}.

10. Derive the formula for the volume of a sphere by integrating over the interior of a sphere of radius a with a surface given by $r = a$.

11. Derive the formula for the volume of a right circular cylinder of radius a and height h.

12. Find the volume of a cup obtained by rotating the parabola

$$z = 4.00\rho^2$$

around the z axis and cutting off the top of the paraboloid of revolution at $z = 4.00$.

13. Find the volume of a right circular cylinder of radius $a = 4.00$ with a paraboloid of revolution scooped out of the top of it such that the top surface is given by

$$z = 10.00 + 1.00\rho^2$$

and the bottom surface is given by $z = 0.00$.

14. Find the volume of a solid with vertical walls such that its base is a square in the x–y plane defined by $0 \le x \le 2.00$ and $0 \le x \le 2.00$ and its top is defined by the plane $z = 20.00 + x + y$.

15. Find the volume of a solid produced by scooping out the interior of a circular cylinder of radius 10.00 cm and height 12.00 cm so that the inner surface conforms to $z = 2.00\ \mathrm{cm} + (0.01000\ \mathrm{cm}^{-2})\rho^3$.

16. Find the moment of inertia of a ring with radius 10.00 cm, width 0.25 cm, and a mass of 0.100 kg.

17. Find the moment of inertia of a flat rectangular plate with dimensions 0.500 m by 0.400 m around an axis through the center of the plate and perpendicular to it. Assume that the plate has a mass $M = 2.000$ kg and that the mass is uniformly distributed.

18. Find the volume of a circular cylinder of radius 0.1000 m centered on the z axis, with a bottom surface given by the x–y plane and a top surface given by $z = 0.1000\ \text{m} + 0.0500y$.

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Chapter 10

Mathematical Series

Principal Facts and Ideas

- A mathematical series is a sum of terms, either with a finite number of terms or an infinite number of terms.
- A constant series has terms that are constants, and a functional series has terms that are constants times functions.
- An infinite series converges if the sum approaches a finite limit ever more closely as ever more terms are summed.
- A Maclaurin series is a functional series with basis functions that are power of x, where x is the independent variable.
- A Taylor series is a functional series with basis functions that are powers of $x - h$, where h is a constant.
- An infinite power series can represent a function within a region inside which it converges.

Objectives

After studying this chapter, you should be able to:

- determine whether an infinite constant series converges,
- determine how large a partial sum must be taken to approximate a series to a specified accuracy,
- compute the coefficients for a power series to represent a given function,
- determine the region of convergence of a power series.

10.1 CONSTANT SERIES

A *sequence* is a set of numerical quantities with a rule for generating one member of the set from the previous member. If the members of a sequence are added together, the result is a *series*. A *finite series* has a finite number of terms, and an *infinite series* has an infinite number of terms. If a series has terms that are constants, it is a *constant series*. Such a series can be written

$$s = a_0 + a_1 + a_2 + a_3 + a_4 + \cdots + a_n + \cdots \qquad (10.1)$$

For an infinite series, we define the nth *partial sum* as the sum of the first n terms:

$$S_n = a_0 + a_1 + a_2 + a_3 + \cdots + a_{n-1} = \sum_{k=0}^{n-1} a_k. \qquad (10.2)$$

The infinite series is the limit

$$s = \lim_{n\to\infty} S_n. \qquad (10.3)$$

If this limit exists and is finite, we say that the series *converges*. If the magnitude of S_n becomes larger and larger without bound as n becomes large, or if S_n continues to oscillate without approaching a fixed value as n becomes large, we say that the series *diverges*.

We ask two questions about an infinite constant series:

1. Does the series converge?
2. What is the value of the series if it does converge?

There is no general method for finding the value of every convergent infinite series, but some series can be summed by finding an appropriate method.[1] If you cannot find a method to sum a particular infinite series, you might be able to approximate a convergent series with a partial sum.

[1] See A.D. Wheelon, "On the Summation of Infinite Series," *J. Appl. Phys.*, **25**, 113 (1954), for a method that can be applied to a large number of series.

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00010-0

10.1.1 Some Convergent Constant Series

A well-known convergent constant series is

$$s = 1 + \frac{1}{2} + \frac{1}{4} + \frac{1}{8} + \cdots + \frac{1}{2^n} + \cdots = \sum_{n=0}^{\infty} \frac{1}{2^n}. \quad (10.4)$$

Example 10.1. Find the value of the series in Eq. (10.4). We write the sum as the first term plus the other terms, with a factor of $\frac{1}{2}$ factored out of all the other terms:

$$s = 1 + \frac{1}{2}\left(1 + \frac{1}{2} + \frac{1}{4} + \frac{1}{8} + \cdots\right).$$

The series in parentheses is just the same as the original series. There is no problem due to the apparent difference that the series in parentheses seems to have one less term than the original series, because both series have an infinite number of terms. We now write

$$s = 1 + \frac{1}{2}s,$$

which can be solved to give

$$s = 2.$$

Exercise 10.1. Show that in the series of Eq. (10.4) any term of the series is equal to the sum of all the terms following it. (Hint: Factor a factor out of all of the following terms so that they will equal this factor times the original series, whose value is now known.)

The result of this exercise is of interest in seeing how a series can be approximated by a partial sum. For the series of Eq. (10.4), any term is equal to the sum of all following terms, so we can write

$$s = S_n + a_{n-1}. \quad (10.5)$$

It is easy to determine the difference between the entire sum and a partial sum using this equation. With some other convergent infinite series, we might try to apply Eq. (10.5) as a rough measure of the error in approximating s by S_n.

Example 10.2. Determine which partial sum approximates the series of Eq. (10.4) to

(a) 1%.

Since 1% of 2 is equal to 0.02, we find the first term of the series that is equal to or smaller than 0.02, and take the partial sum that ends with that term. The remaining terms are equal to that term. We have

$$\frac{1}{2^6} = \frac{1}{64} = 0.015625,$$

so that the partial sum required is the one ending with $\frac{1}{64}$, or S_7. Its value is

$$S_7 = 1.984375.$$

(b) 0.001%.

Since 0.001% of 2 is 2×10^{-5} , and $1/2^n$ has the value 1.5259×10^{-5} when $n = 16$, we need the partial sum S_{17}, which has the value $S_{17} = 1.999984741$.

Exercise 10.2. Consider the series

$$s = 1 + \frac{1}{2^2} + \frac{1}{3^2} + \frac{1}{4^2} + \cdots + \frac{1}{n^2} + \cdots$$

which is known to be convergent and to equal $\pi^2/6 = 1.64993\cdots$. Using Eq. (10.5) as an approximation, determine which partial sum approximates the series to

(a) 1%.
(b) 0.001%.

How good are these approximations?

10.1.2 The Geometric Series

The series of Eq. (10.4) is an example of a *geometric series*, which is defined to be

$$\begin{aligned} s &= a + ar + ar^2 + ar^3 + ar^4 + \cdots + ar^n + \cdots \\ &= a\left(1 + r + r^2 + r^3 + \cdots + r^n + \cdots\right), \\ &= a\sum_{n=0}^{\infty} r^n, \end{aligned} \quad (10.6)$$

where a and r are constants. In order for the infinite series of Eq.(10.6) to converge, the magnitude of r must be less than unity. Otherwise, each term would be equal to or larger than the previous term, causing the sum to grow without bound (diverge) as more and more terms are added. However, r can be positive or negative. If r is negative, the sum has terms of alternating sign, but still converges only if $|r| < 1$.

The value of a geometric series can be obtained in the same way as was the value of the series in Eq. (10.4),

$$s = a + r(a + ar + ar^2 + ar^3 + \cdots) = a + rs$$

or

$$\boxed{s = \frac{a}{1 - r}} \quad (|r| < 1). \quad (10.7)$$

The partial sums of the geometric series are given by

$$\boxed{\begin{aligned} S_n &= a + ar + ar^2 + \cdots + ar^{n-1} \\ &= a\sum_{n=0}^{n-1} r^n = a\frac{1 - r^n}{1 - r} \end{aligned}}. \quad (10.8)$$

Equation (10.8) is valid for any value of r, since a finite series always converges.

Example 10.3. The molecular partition function z is defined in the statistical mechanics of noninteracting molecules as the sum following over all the states of one molecule

$$z = \sum_{i=0}^{\infty} \exp\left(\frac{-E_i}{k_B T}\right),$$

where i is an index specifying the state, E_i is the energy that the molecule has when in state number i, k_B is Boltzmann's constant, equal to $1.3806568 \times 10^{-23}$ J K^{-1}, and T is the absolute (Kelvin) temperature. If we consider only the vibration of a diatomic molecule, to a good approximation

$$E_i = E_v = h\nu\left(v + \frac{1}{2}\right),$$

where ν is the vibrational frequency, v is the vibrational quantum number, which can take on all nonnegative integral values, and h is Planck's constant, equal to 6.6261×10^{-34} J s. Use Eq. (10.7) to find an expression for the vibrational partition function.

$$\begin{aligned} z_{vib} &= \sum_{v=0}^{\infty} \exp\left[\frac{-h\nu\left(v + \frac{1}{2}\right)}{k_B T}\right] \\ &= \exp\left(\frac{-h\nu}{2k_B T}\right) \sum_{v=0}^{\infty} \left[\exp\left(\frac{h\nu}{k_B T}\right)\right]^v \\ &= e^{-x/2} \sum_{v=0}^{\infty} \left(e^{-x}\right)^v, \end{aligned}$$

where we let $h\nu/k_B T = x$, a positive quantity. The sum is a geometric series, so

$$z_{vib} = \frac{e^{-x/2}}{1 - e^{-x}} = \frac{e^{-h\nu/2k_B T}}{1 - e^{-h\nu/k_B T}}.$$

The series is convergent, because e^{-x} is smaller in magnitude than unity for all positive values of x.

Exercise 10.3. Find the value of the infinite series

$$\sum_{n=0}^{\infty} [\ln(2)]^n.$$

Determine how well this series is approximated by S_2, S_5, S_{10}, and S_{20}.

10.1.3 The Harmonic Series

The *harmonic series* is defined to be

$$s = 1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \cdots + \frac{1}{n} + \cdots \tag{10.9}$$

Here are a few partial sums of this series:

$$\begin{aligned} S_1 &= 1, \\ S_2 &= 1.5, \\ S_{200} &= 6.87803, \\ S_{1000} &= 8.48547, \\ S_{100,000} &= 13.0902. \end{aligned}$$

The harmonic series is known to diverge

$$s = \lim_{n \to \infty} S_n = \infty. \tag{10.10}$$

It might appear that this series would converge, because the terms keep on getting smaller as you go further into the series. This is a necessary condition for a series to converge, but it is not sufficient. If a series does not approach a finite value as more and more terms are taken, it is divergent. We will show that the harmonic series is divergent when we introduce tests for convergence.

Exercise 10.4. Evaluate the first 20 partial sums of the harmonic series.

There are a number of constant series listed in Appendix C.

10.1.4 Tests for Convergence

There are several tests that will usually tell us whether an infinite series converges:

- *The Comparison Test*. If a series has terms each of which is smaller in magnitude than the corresponding term of a convergent series, it is convergent. If a series has terms each of which is larger in magnitude than the corresponding term of a divergent series, it is divergent.
- *The Alternating Series Test*. If a series has terms that alternate in sign, it is convergent if the terms approach zero as you go further and further into the series and if each term is smaller in magnitude than the previous term.
- The *nth-Term Test.* If the terms of a series approach some limit other than zero or do not approach any limit as you go further into the series, the series diverges.
- *The Integral Test.* If a formula can be written to deliver the terms of a series

  $$a_n = f(n), \tag{10.11}$$

  then the series will converge if the improper integral

  $$\int_1^{\infty} f(x)\mathrm{d}x \tag{10.12}$$

  converges and will diverge if the improper integral diverges.

- *The Ratio Test.* For a series of positive terms or a series of negative terms, we define the limit

$$r = \lim_{n\to\infty} \frac{a_{n+1}}{a_n}. \tag{10.13}$$

If $r < 1$, the series converges. If $r > 1$, the series diverges. If $r = 1$, the test fails, and the series might either converge or diverge. If the ratio does not approach any limit but does not increase without bound, the test also fails.

Example 10.4. Apply the ratio test and the integral test to the harmonic series.

Apply the ratio test:

$$r = \lim_{n\to\infty} \left[\frac{1/n}{1/(n-1)} \right] = \lim_{n\to\infty} \frac{n-1}{n} = 1.$$

The ratio test fails. Apply the integral test:

$$\int_1^0 \frac{1}{x} \mathrm{d}x = \ln(x)\Big|_1^\infty = \lim_{b\to\infty} [\ln(b) - \ln(1)] = \infty.$$

The series diverges by the integral test.

Exercise 10.5. Show that the geometric series converges if $r^2 \prec 1$.

Example 10.5. Determine whether the series converges:

$$s = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \cdots = \sum_{n-1}^{\infty} \frac{(-1)^{n-1}}{n}.$$

This is an alternating series, so the alternating series test applies. Since every term approaches more closely to zero than the previous term, the series is convergent.

Example 10.6. Determine whether the series converges:

$$s = 1 - \frac{1}{2} + \frac{2}{2} - \frac{1}{3} + \frac{2}{3} - \frac{1}{4} + \frac{2}{4} - \frac{1}{5} + \frac{2}{5} - \cdots$$

This is a tricky series, because it is an alternating series, and the nth term approaches zero as n becomes large. However, the series diverges. The alternating series test does not apply, because it requires that each term be closer to zero than the previous term. Half the time as you go from one term to the next in this series, the magnitude increases instead of decreasing. Let us manipulate the series by subtracting each negative term from the following positive term to obtain

$$s = 1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \frac{1}{5} + \cdots$$

This is the harmonic series, which we already found to diverge.

Exercise 10.6. Test the following series for convergence:

$$\sum_{n=1}^{\infty} \frac{1}{n^2}.$$

10.2 POWER SERIES

A *functional series* has the form

$$s(x) = a_0 g_0(x) + a_1 g_1(x) + a_2 g_2(x) + a_3 g_3(x) + \cdots \tag{10.14}$$

if there is a single independent variable, x. The set of constants $a_0, a_1, a_2, \ldots$ are called *coefficients* and the set of functions $g_0, g_1, g_2, g_3, \ldots$ are called *basis functions*. An infinite functional series might converge for some values of x and diverge for others. If there is an interval of values of x such that the series converges for all values of x in that interval, we say that the series is *convergent in that interval*. There is an important mathematical concept called *uniform convergence*. A functional series is uniformly convergent in an interval if it converges with at least a certain fixed rate of convergence in the entire interval. We do not discuss the details of this concept.[2] If a functional series is uniformly convergent in some interval, it has been shown to have some useful mathematical properties, which we discuss later. There are two problems to be faced in constructing a series to represent a given function. The first is finding the values of the coefficients so that the function will be correctly represented. The second is finding the interval in which the series is convergent.

10.2.1 Maclaurin Series

The most common type of functional series is the *power series,* which uses powers of the independent variable as basis functions. The first type of power series is the *Maclaurin series*:

$$f(x) = s(x) = a_0 + a_1 x + a_2 x^2 + \cdots \tag{10.15}$$

where $f(x)$ is the function to be represented and $s(x)$ stands for the series. We now need to determine the a coefficients. In order for the function and the series to be equal at all values of x in some interval including $x = 0$, they must be equal at $x = 0$, which means that all of the terms in the series vanish except for the first term:

$$\boxed{f(0) = s(0) = a_0}. \tag{10.16}$$

This determines a_0. In order to represent a function by a power series, we require that the function and all of its derivatives are differentiable at $x = 0$. Such a function is said to be *analytic* at $x = 0$. We now require that all derivatives of the function and of the series be equal at $x = 0$. The nth derivative of the series at $x = 0$ is

$$\left(\frac{\mathrm{d}^n s}{\mathrm{d}x^n} \right)_{x=0} = n! a_n, \tag{10.17}$$

[2] David Bressoud, *A Radical Approach to Real Analysis*, pp. 191–194, Math. Assoc. of America, Washington, DC, 1994.

where $n!$ (n factorial) is defined for $n \geq 1$ as the product of all whole numbers up to and including n:

$$n! = n(n-1)(n-2)\cdots(3)(2)(1). \tag{10.18}$$

We also define 0! to equal 1. Equating the derivatives of the function and the series at $x = 0$ gives a general formula for the coefficients in a Maclaurin series to represent the function $f(x)$:

$$\boxed{a_n = \frac{1}{n!}\left(\frac{\mathrm{d}^n f}{\mathrm{d}x^n}\right)_{x=0} \quad (n = 1,2,3,\ldots)}. \tag{10.19}$$

The subscript $x = 0$ on the derivative symbol indicates that the derivative is to be evaluated at $x = 0$. A power series that is obtained by using Eq. (10.19) to obtain the coefficients faithfully represents the appropriate function in the vicinity of $x = 0$ if it converges and if infinitely many terms are taken. However, we must determine how far from $x = 0$ we can go and still represent the function by the series.

Example 10.7. Find all of the coefficients for the Maclaurin series representing $\sin(x)$.

Since $\sin(\theta) = 0$,

$$a_0 = 0,$$
$$a_1 = \left[\frac{\mathrm{d}}{\mathrm{d}x}\sin(x)\right]_0 = \cos(0) = 1,$$

where the subscript indicates that the derivative is evaluated at $x = 0$. The second partial sum of the series is therefore

$$S_2 = 0 + x = x$$

giving the same approximation as in Eq. (2.37). Figure 10.1 shows the function $\sin(x)$ and the approximation, $S_2 = x$. The derivatives of $\sin(x)$ follow a repeating pattern:

$$\begin{aligned} f(x) &= \sin(x), \\ \frac{\mathrm{d}f}{\mathrm{d}x} &= \cos(x), \\ \frac{\mathrm{d}^2 f}{\mathrm{d}x^2} &= -\sin(x), \\ \frac{\mathrm{d}^3 f}{\mathrm{d}x^3} &= -\cos(x), \\ \frac{\mathrm{d}^4 f}{\mathrm{d}x^4} &= \sin(x). \end{aligned}$$

When these are evaluated at $x = 0$, all of the even-numbered derivatives vanish, and the odd-numbered derivatives are alternately equal to 1 and -1:

$$\sin(x) = x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 - \frac{1}{7!}x^7 + \cdots$$

Exercise 10.7. Show that the Maclaurin series for e^x is

$$e^x = 1 + \frac{1}{1!}x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \frac{1}{4!}x^4 + \cdots \tag{10.20}$$

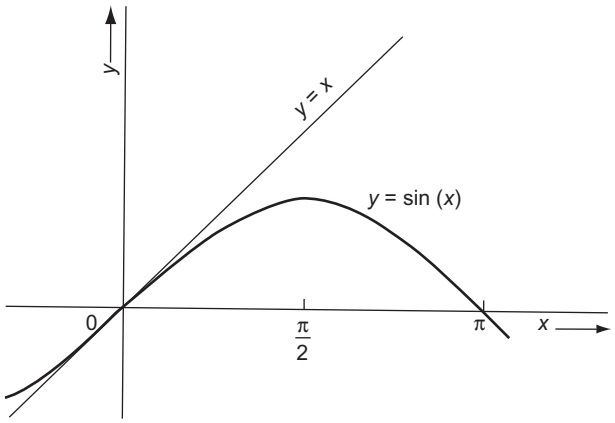


FIGURE 10.1 The function $\sin(x)$ and the approximation $S_2 = x$.

10.2.2 Taylor Series

A Taylor series has the form

$$s(x) = a_0 + a_1(x-h) + a_2(x-h)^2 + a_3(x-h)^3 + \cdots$$

where $h \neq 0$. We say that the function is *expanded* around $x = h$. There are a number of important functions that are not differentiable at $x = 0$, and these cannot be represented by a Maclaurin series, but can be represented by a Taylor series. One such function is $\ln(x)$. The first derivative of this function is $1/x$, which becomes infinite as $x \to 0$, as do the other derivatives. Although there is no Maclaurin series for $\ln(x)$, we can find a Taylor series for a positive value of h.

In order to find the coefficients for a Taylor series, we require the function and the series to be equal at $x = h$ and to have the same derivatives of all orders at $x = h$. This gives

$$\boxed{a_0 = f(h); \quad a_n = \frac{1}{n!}\left(\frac{\mathrm{d}^n f}{\mathrm{d}x^n}\right)_{x=h}}, \tag{10.21}$$

where $f(x)$ is the function to be represented and the subscript $x = h$ indicates that the derivative is to be evaluated at $x = h$.

Example 10.8. Find the Taylor series for $\ln(x)$, expanding about $x = 1$.

The series is

$$\ln(x) = a_0 + a_1(x-1) + a_2(x-1)^2 + a_3(x-1)^3 + \cdots$$

The first term is determined by letting $x = 1$, in which case all of the terms except a_0 vanish:

$$a_0 = \ln(1) = 0.$$

The first derivative of $\ln(x)$ is $1/x$, which equals 1 at $x = 1$. The second derivative is $-1/x^2$, which equals -1 at $x = 1$.

The third derivative is $2/x^3$, which equals 2 at $x = 1$. The derivatives follow a regular pattern,

$$\left(\frac{\mathrm{d}^n f}{\mathrm{d}x^n}\right)_{x=1} = (-1)^{n-1}\left.\frac{(n-1)!}{x^n}\right|_{x=1} = (-1)^{n-1}(n-1)!$$

so that

$$\frac{1}{n!}\left(\frac{\mathrm{d}^n f}{\mathrm{d}x^n}\right)_{x=1} = \frac{(-1)^{n-1}}{n}$$

and

$$\ln(x) = (x-1) - \frac{1}{2}(x-1)^2 + \frac{1}{3}(x-1)^3 - \frac{1}{4}(x-1)^4 + \cdots$$

Exercise 10.8. Find the Maclaurin series for $\ln(1+x)$. You can save some work by using the result of the previous example.

10.2.3 The Convergence of Power Series

If a series is to represent a function $f(x)$ in some interval, it must be convergent in the entire interval and must converge to the value of the function for every value of x in the interval. For a fixed value of x, the series $s(x)$ is no different from a constant series, and all the tests for convergence of Section 10.1 can be applied. We can consider different fixed values of x and determine the *interval of convergence*, the interval in which the series is convergent.

Example 10.9. Investigate the convergence of the Taylor series for $\ln(x)$ in the previous example.

We consider three cases: $x = 1$, $x > 1$, and $x < 1$. If $x = 1$, the entire series vanishes, as does the function, so the series converges to the value of $\ln(x)$ for $x = 1$. For $x > 1$, the series is an alternating series, and we can apply the alternating series test. The nth term of the series is

$$t_n = a_n(x-1)^n = \frac{(x-1)^n(-1)^{n-1}}{n}.$$

Look at the limit of this as n becomes large:

$$\lim_{n\to\infty} t_n = \begin{cases} 0 & \text{if } |x-1| \le 1 \text{ or } 0 \le x \le 2, \\ \infty & \text{if } |x-1| > 1 \text{ or } x > 2. \end{cases}$$

Since the series diverges if $x > 2$, the interval of convergence for $x > 1$ extends up to and including $x = 2$. For $x < 1$, the series is not alternating. We apply the ratio test:

$$r = \lim_{n\to\infty}\frac{t_n}{t_{n-1}} = \lim_{n\to\infty}\left[-\frac{(x-1)^n/n}{(x-1)^{n-1}/(n-1)}\right] = -(x-1) = 1-x.$$

This will be less than unity if x lies between 0 and 1, but if $x = 0$, the test fails. However, if $x = 0$, the series is the same as the harmonic series except for the sign, and thus diverges. However, the series does converge for positive values of x close to 0. The interval of convergence is $0 < x \le 2$.

We summarize the behavior of the Taylor series representation of the previous example: There is a point at which the logarithm function is not analytic, at $x = 0$. The function is analytic to the right of this point, and the series equals the function for positive values arbitrarily close to $x = 0$. Beyond $x = 2$, the series diverges. The interval of convergence is centered on the point about which the function is expanded, which is $x = 1$ in this case. The distance from $x = 1$ to the left end of the interval of convergence is 1 unit, and the distance from $x = 1$ to the right end of the interval of convergence is also 1. This distance is called the *radius of convergence*. Even though the function is defined for values of x beyond $x = 2$, the series does not converge and cannot represent the function for values of x beyond $x = 2$. Another Taylor series expanded about a value of x larger than $x = 1$ can represent the logarithm function beyond $x = 2$.

Exercise 10.9. Find the Taylor series for $\ln(x)$, expanding about $x = 2$, and show that the radius of convergence for this series is equal to 2, so that the series can represent the function in the region $0 < x \le 4$.

The behavior of the Taylor series representation of the logarithm function is typical. In general, the interval of convergence is centered on the point about which we are expanding and extends the same distance in both directions. The radius of convergence is the distance from the point about which we are expanding to the closest point at which the function is not analytic, and the interval of convergence extends by this distance in either direction. If a function is defined on both sides of a point at which the function is not analytic, it is represented on the two sides by different series.

Example 10.10. Find the interval of convergence for the series representing the exponential function in Eq. (10.20).

We apply the ratio test,

$$r = \lim_{n\to\infty}\frac{t_n}{t_{n-1}} = \lim_{n\to\infty}\frac{x^n/n!}{x^{n-1}/(n-1)!} = \lim_{n\to\infty}\frac{x}{n}.$$

This limit vanishes for any real finite value of x, so the series converges for any real finite value of x, and the radius of convergence is infinite.

Exercise 10.10. Find the series for $1/(1-x)$, expanding about $x = 0$. What is the interval of convergence?

Unfortunately, the situation is not always so simple as in the examples we have been discussing. A power series can

represent a function for complex values of the independent variable. A Taylor series converges to the given function in a circle in the Argand plane with radius equal to the radius of convergence. The radius of convergence is the distance from the point about which we expand to the closest point in the complex plane at which the function is not analytic.

For example, if we wanted to construct a Maclaurin series for the function

$$f(x) = \frac{1}{1+x^2}, \tag{10.22}$$

the radius of convergence would be determined by discontinuities at $x = i$ and $x = -i$ even though there are no discontinuities for real values of x. The radius of convergence equals unity, the distance from the origin to $x = \pm i$ in the Argand plane. Therefore, on the real axis, the series converges to the function only for value of x lying between -1 and $+1$. We do not discuss the behavior of power series in the complex plane, but you can read more about this topic in the book by Kreyszig listed at the end of the book.

10.2.4 Power Series in Physical Chemistry

In physical chemistry there are a number of applications of power series, but in most applications, a partial sum is used to approximate the series. For example, the behavior of a nonideal gas is often described by use of the *virial series* or *virial equation of state*,

$$\frac{PV_\mathrm{m}}{RT} = 1 + \frac{B_2}{V_\mathrm{m}} + \frac{B_3}{V_\mathrm{m}^2} + \frac{B_4}{V_\mathrm{m}^3} + \cdots \tag{10.23}$$

where P is the pressure, V_m is the molar volume of the gas, T is the Kelvin temperature, and R is the ideal gas constant. This is a Maclaurin series in the variable $1/V_\mathrm{m}$. The coefficients $B_2, B_3, \ldots$ are called *virial coefficients* and are functions of T but not functions of V_m. If all the virial coefficients were known for a particular gas, the virial series would represent exactly the volumetric behavior of that gas at all positive values of $1/V_\mathrm{m}$. However, only the first few virial coefficients can be determined experimentally or theoretically, so a partial sum must be used. For many purposes, the two-term truncated equation is adequate:

$$\frac{PV_\mathrm{m}}{RT} \approx 1 + \frac{B_2}{V_\mathrm{m}}. \tag{10.24}$$

There is another commonly used series equation of state, sometimes called the *pressure virial equation of state*:

$$PV_\mathrm{m} = RT + A_2P + A_3P^2 + A_4P^3 + \cdots \tag{10.25}$$

This is a Maclaurin series in P. It is also truncated for practical use.

Example 10.11. Show that the coefficient A_2 in Eq. (10.25) is equal to the coefficient B_2 in Eq. (10.23).

We multiply Eq. (10.23) on both sides by RT/V_m to obtain

$$P = \frac{RT}{V_\mathrm{m}} + \frac{RTB_2}{V_\mathrm{m}^2} + \frac{RTB_3}{V_\mathrm{m}^3} + \cdots$$

This must be equal to

$$P = \frac{RT}{V_\mathrm{m}} + \frac{A_2P}{V_\mathrm{m}} + \frac{A_3P^2}{V_\mathrm{m}} + \cdots$$

We convert the second series into a series in $1/V_\mathrm{m}$ by substituting the first series into the right-hand side wherever a P occurs. When the entire series on the right-hand side of the virial equation is squared, every term will have at least a V_m^2 in the denominator [see Eq. (5) of Appendix C for the square of a series]. Therefore,

$$P = \frac{RT}{V_\mathrm{m}} + \frac{A_2}{V_\mathrm{m}}\left(\frac{RT}{V_\mathrm{m}} + \frac{RTB_2}{V_\mathrm{m}^2} + \cdots\right) + O\left(\frac{1}{V_\mathrm{m}}\right)^3,$$

where the symbol $O(1/V_\mathrm{m})^3$ ("order of $(1/V_\mathrm{m})^3$") stands for terms of degree $(1/V_\mathrm{m})^3$ or higher.

We now have

$$P = \frac{RT}{V_\mathrm{m}} + \frac{RTA_2}{V_\mathrm{m}^2} + O\left(\frac{1}{V_\mathrm{m}}\right)^3.$$

If two power series in the same independent variable are equal to each other for all values of the independent variable, then any coefficient in one series is equal to the corresponding coefficient of the other series.

Comparison of the two expressions for P shows that

$$B_2 = A_2.$$

Exercise 10.11. Find the relationship between the coefficients A_3 and B_3.

Another application of a power series in physical chemistry is in the discussion of *colligative properties* (freezing-point depression, boiling-point elevation, and osmotic pressure). If X_1 is the mole fraction of solvent, $\Delta_\mathrm{vap}H_m$ is the molar heat of vaporization of the solvent, T_0 is the pure solvent's boiling temperature, and T is the solution's boiling temperature, it is shown in physical chemistry textbooks that

$$-\ln(X_1) = \frac{\Delta_\mathrm{vap}H_m}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right). \tag{10.26}$$

If there is only one *solute* (component other than the solvent), then its mole fraction, X_2, is given by

$$X_2 = 1 - X_1. \tag{10.27}$$

The logarithm on the left-hand side of Eq. (10.26) is represented by the power series

$$-\ln(X_1) = -\ln(1 - X_2) = X_2 + \frac{1}{2}X_2^2 + \cdots \tag{10.28}$$

If X_2 is not too large, we can truncate this series after one term and write

$$X_2 \approx \frac{\Delta_{\text{vap}} H_m}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right). \tag{10.29}$$

Exercise 10.12. Determine how large X_2 can be before the truncation of Eq. (10.28) that was used in Eq. (10.29) is inaccurate by more than 1%.

10.3 MATHEMATICAL OPERATIONS ON SERIES

Carrying out operations such as differentiation and integration on an infinite functional series involves questions about convergence and whether differentiating or integrating each term and then summing the result gives the same result as first summing the series and then differentiating or integrating. Although we do not prove it, the principal fact is: *If a series is uniformly convergent, the result of operating on the series is the same as the result of operating on the individual terms and then summing the resulting series*. For example, consider a general functional series:

$$f(x) = \sum_{n=0}^{\infty} a_n g_n(x). \tag{10.30}$$

If the series is uniformly convergent, then

$$\frac{\mathrm{d}f}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}x}\left[\sum_{n=0}^{\infty} a_n g_n(x)\right] = \sum_{n=0}^{\infty} a_n \frac{\mathrm{d}g_n}{\mathrm{d}x}. \tag{10.31}$$

This amounts to interchange of the operations of summing and differentiating. Similarly, for a uniformly convergent series,

$$\begin{aligned}\int_b^c f(x)\mathrm{d}x &= \int_b^c \left[\sum_{n=0}^{\infty} a_n g_n(x)\right]\mathrm{d}x \\ &= \sum_{n=0}^{\infty} a_n \int_b^c g_n\left(x\right)\mathrm{d}x.\end{aligned} \tag{10.32}$$

Example 10.12. Find the Maclaurin series for $\cos(x)$ from the Maclaurin series for $\sin(x)$.

The series is uniformly convergent for all values of x, so we can interchange the order of summing and differentiating. The series for $\sin(x)$ was given in a previous example:

$$\sin(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots,$$

so that

$$\begin{aligned}\frac{\mathrm{d}\left[\sin(x)\right]}{\mathrm{d}x} &= \cos(x) = 1 - \frac{3x^2}{3!} + \frac{5x^4}{5!} - \frac{7x^6}{7!} + \cdots \\ &= 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots\end{aligned}$$

which is the known series expression for $\cos(x)$.

Exercise 10.13. From the Maclaurin series for $\ln(1+x)$

$$\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \cdots$$

find the Taylor series for $1/\left(1+x\right)$, using the fact that

$$\frac{\mathrm{d}\left[\ln(1+x)\right]}{\mathrm{d}x} = \frac{1}{1+x}.$$

For what values of x is your series valid?

10.4 POWER SERIES WITH MORE THAN ONE INDEPENDENT VARIABLE

If $f(x,y)$ represents a function of x and y, under certain conditions a power series representation can be found. If the function possesses all of its derivatives at $x = 0, y$, we can write

$$\begin{aligned}f(x,y) = {} & a_{00} + a_{10}x + a_{01}y + a_{11}xy + a_{20}x^2 + a_{02}y^2 \\ & + a_{21}x^2y + a_{12}xy^2 + a_{22}x^2y^2 + \cdots\end{aligned} \tag{10.33}$$

We find the coefficient a_{00} by requiring that the function and the series representation are equal to each other at $x = 0$ and $y = 0$:

$$f(0,0) = a_{00}. \tag{10.34}$$

We require that the first derivatives of the function and the series are equal to each other at $x = 0,\ y = 0$

$$\left(\frac{\partial f}{\partial x}\right)_y = a_{10} + a_{11}y + 2a_{21}xy + a_{12}y^2 + 2a_{22}xy^2 + \cdots \tag{10.35}$$

When this is evaluated at $x = 0,\ y = 0$

$$\left(\frac{\partial f}{\partial x}\right)_y\Bigg|_{0,0} = a_{10}, \tag{10.36}$$

where the subscripts 0,0 indicate the values of x and y for which the derivative is evaluated. Similarly,

$$\left(\frac{\partial f}{\partial y}\right)_x\Big|_{0,0} = a_{01}. \tag{10.37}$$

From the mixed second derivative, we can deduce

$$\left(\frac{\partial^2 f}{\partial y \partial x}\right)\Big|_{0,0} = a_{11}. \tag{10.38}$$

The general pattern involves higher partial derivatives

$$\frac{1}{n!m!}\left(\frac{\partial^{n+m} f}{\partial^m y \partial^n x}\right)\Big|_{0,0} = a_{nm}. \tag{10.39}$$

Example 10.13. Find the first few terms of the Maclaurin series representing the function $f(x,y) = \exp(x+y) = e^{x+y}$. Compare your result with the product of the Maclaurin series representing e^x and the series representing e^y.

$$\begin{aligned}
f(x,y) = e^{x+y} &= a_{00} + a_{10}x + a_{01}y + a_{11}xy \\
&\quad + a_{21}x^2y + a_{12}xy^2 + a_{22}x^2y^2 + \cdots \\
a_{00} &= 1, \\
a_{10} &= \left(\frac{\partial e^{xy}}{\partial x}\right)_y\Big|_{0,0} = e^{x+y}|_{0,0} = 1, \\
a_{01} &= \left(\frac{\partial e^{xy}}{\partial y}\right)_y\Big|_{0,0} = e^{x+y}|_{0,0} = 1, \\
a_{11} &= \frac{1}{1!1!}\left(\frac{\partial^2 e^{x+y}}{\partial y \partial x}\right)\Big|_{0,0} = \frac{\partial e^{x+y}}{\partial y}\Big|_{0,0} = 1.
\end{aligned}$$

All the derivatives are equal to e^{x+y}. which gives unity when evaluated at $x = 0$, $y = 0$.

$$\begin{aligned}
a_{nm} &= \frac{1}{n!m!}, \\
e^{x+y} &= 1 + \frac{1}{1!0!}x + \frac{1}{0!1!}y + \frac{1}{1!1!}xy \\
&\quad + \frac{1}{2!0!}x^2 + \frac{1}{0!2!}y^2 + \cdots
\end{aligned}$$

The product of the two series for e^x and e^y is

$$\begin{aligned}
&\left(1 + \frac{1}{1!}x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \frac{1}{4!}x^4 + \cdots\right) \\
&\quad \left(1 + \frac{1}{1!}y + \frac{1}{2!}y^2 + \frac{1}{3!}y^3 + \frac{1}{4!}y^4 + \cdots\right) \\
&\quad = 1 + \frac{1}{1!0!}x + \frac{1}{0!1!}y + \frac{1}{1!1!}xy + \frac{1}{2!0!}x^2 \\
&\qquad + \frac{1}{0!2!}y^2 + \cdots
\end{aligned}$$

The same as the two-dimensional series.

Exercise 10.14. Find the formulas for the coefficients in a Taylor series that expands the function $f(x,y)$ around the point $x = a, y = b$.

Problems

1. Test the following series for convergence

$$\sum_{n=0}^{\infty}\left((-1)^n\left(n-1\right)/n^2\right).$$

2. Test the following series for convergence

$$\sum_{n=0}^{\infty}\left((-1)^n n/n!\right).$$

Note: $n! = n(n-1)(n-2)\cdots(2)(1)$ for positive integral values of n and $0! = 1$.

3. Test the following series for convergence

$$\sum_{n=0}^{\infty}\left(1/n!\right).$$

4. Find the Maclaurin series for $\cos(x)$.

5. Find the Taylor series for $\cos(x)$, expanding about $x = \pi/2$.

6. By use of the Maclaurin series already obtained in this chapter, prove the identity $e^{ix} = \cos(x) + i\sin(x)$.

7. Show that no Maclaurin series

$$f(x) = a_0 + a_1x + a_2x^2 + \cdots$$

can be formed to represent the function $f(x) = \sqrt{x}$. Why is this?

8. Find the first few coefficients for the Maclaurin series for the function

$$f(x) = \sqrt{1+x}.$$

9. Find the coefficients of the first few terms of the Taylor series

$$\sin(x) = a_0 + a_1\left(x - \frac{\pi}{4}\right) + a_2\left(x - \frac{\pi}{4}\right)^2 + \cdots,$$

where x is measured in radians. What is the radius of convergence of the series?

10. Find the coefficients of the first few terms of the Maclaurin series

$$\sinh(x) = a_0 + a_1x + a_2x^2 + \cdots$$

What is the radius of convergence of the series?

11. The sine of $\pi/4$ radians (45°) is $\sqrt{2}/2 = 0.70710678\ldots$ How many terms in the series

$$\sin(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \ldots$$

must be taken to achieve 1% accuracy at $x = \pi/4$?

12. The cosine of 30° ($\pi/6$ radians) is equal to $\sqrt{3}/2 = 0.866025\ldots$ How many terms in the series

$$\cos(x) = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots$$

must be taken to achieve 0.1% accuracy $x = \pi/6$?

13. Estimate the largest value of x that allows e^x to be approximated to 1% accuracy by the following partial sum:

$$e^x \approx 1 + x.$$

14. Estimate the largest value of x that allows e^x to be approximated to 0.01% accuracy by the following partial sum:

$$e^x \approx 1 + x + \frac{x^2}{2!}.$$

15. Find two different Taylor series to represent the function

$$f(x) = \frac{1}{x}$$

such that one series is

$$f(x) = a_0 + a_1(x-1) + a_2(x-1)^2 + \cdots$$

and the other is

$$f(x) = b_0 + b_1(x-2) + b_3(x-2)^2 + \cdots$$

Show that $b_n = a_n/2^n$ for any value of n. Find the interval of convergence for each series (the ratio test may be used). Which series must you use in the vicinity of $x = 3$? Why?

16. Find the Taylor series in powers of $(x - 5)$ that represents the function $\ln(x)$.

17. Using the Maclaurin series for e^x, show that the derivative of e^x is equal to e^x.

18. Find the Maclaurin series that represents $\cosh(x)$. What is its radius of convergence?

19. Find the Taylor series for $\sin(x)$, expanding around $\pi/2$.

20. Find the interval of convergence for the series for $\sin(x)$.

21. Find the interval of convergence for the series for $\cos(x)$.

22. Prove the following fact about power series: If two power series in the same independent variable are equal to each other for all values of the independent variable, then any coefficient in one series is equal to the corresponding coefficient of the other series.

23. Using the Maclaurin series, show that

$$\int_0^{x_1} e^s \, \mathrm{d}x = e^x\big|_0^{x_1} = e^{x_1} - 1.$$

24. Using the Maclaurin series, show that

$$\int_0^{x_1} \cos(ax)\mathrm{d}x = \frac{1}{a}\sin(x)\Big|_0^{x_1} = \frac{1}{a}\sin(ax_1).$$

25. Find the first few terms of the two-variable Maclaurin series representing the function $f(x,y) = \sin(x+y)$.

26. Find the first few terms of the two-variable Taylor series:

$$\ln(xy) = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} a_{mn}(x-1)^n(y-1)^m.$$

Chapter 11

Functional Series and Integral Transforms

Principal Facts and Ideas

- A Fourier series is an infinite series of terms that consist of coefficients times sine and cosine functions. It can represent almost any periodic function. The sine and cosine functions can be replaced by complex exponential functions.
- A Fourier transform is a representation of a function as an integral instead of a sum. Many modern instruments use Fourier transforms to produce spectra from raw data in another form.
- A Laplace transform is a representation of a function that is similar to a Fourier transform except that it uses real exponential functions instead of complex exponential functions.

Objectives

After studying this chapter, you should be able to:

- determine the coefficients of a Fourier series to represent some elementary functions,
- determine the Fourier transform of some elementary functions,
- determine the Laplace transform of some elementary functions,
- manipulate Laplace transforms using various theorems.

11.1 FOURIER SERIES

Fourier series are functional series that use sines and cosines as basis functions.[1] A Fourier series has the form

$$f(x) = a_0 + \sum_{n=1}^{\infty} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{\infty} b_n \sin\left(\frac{n\pi x}{L}\right). \tag{11.1}$$

The sine and cosine functions are periodic functions with period 2π:

$$\sin(x) = \sin(x + 2\pi n), \tag{11.2}$$

$$\cos(x) = \cos(x + 2\pi n), \tag{11.3}$$

and the Fourier series can represent periodic functions.

Exercise 11.1. Using trigonometric identities, show that the basis functions in the series in Eq. (11.1) are periodic with period $2L$.

Fourier series can represent the constructive and destructive *interference* of standing waves in a vibrating string.[2] This fact provides a useful way of thinking about Fourier series. A periodic function of arbitrary shape is represented as a Fourier series by adding up sine and cosine functions with shorter and shorter wavelengths, having different amplitudes adjusted to represent the function correctly. This is analogous to the constructive and destructive interference of waves resulting from the addition of their displacements.

A set of basis functions is said to be *complete* for representation of a set of functions if a series in these functions can exactly represent any function from the set. Fourier proved that the set of sine and cosine basis functions in Eq. (11.1) is a complete set for the representation of periodic functions of period $2L$. He also proved that a Fourier series in x is uniformly convergent for all real values of x.

11.1.1 Finding the Coefficients of a Fourier Series—Orthogonality

To find the coefficients in a Fourier series, we use a property of the basis functions called *orthogonality*. This property is

[1] Fourier series are named for their inventor, Jean Baptiste Joseph Fourier (1768–1730), a famous French mathematician and physicist.

[2] Robert G. Mortimer. Physical Chemistry, 3rd ed., p. 635.

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00011-2

expressed by the three equations:

$$\int_{-L}^{L} \cos\left(\frac{m\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x = L\delta_{mn} = \begin{cases} L & \text{if } m = n, \\ 0 & \text{if } m \neq n, \\ 2L & \text{if } m = n = 0, \end{cases} \tag{11.4}$$

$$\int_{-L}^{L} \cos\left(\frac{m\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)\mathrm{d}x = 0 \text{ for all } m \text{ and } n, \tag{11.5}$$

$$\int_{-L}^{L} \sin\left(\frac{m\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)\mathrm{d}x = \begin{cases} L & \text{if } m = n, \\ 0 & \text{if } m \neq n, \\ 0 & \text{if } m = n = 0. \end{cases} \tag{11.6}$$

These equations can be expressed in terms of the quantity δ_{mn}, which is called the *Kronecker delta*.

$$\delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \quad \text{(definition)}, \tag{11.7}$$

$$\int_{-L}^{L} \cos\left(\frac{m\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x = L\delta_{mn} = \begin{cases} \delta_{mn}L & \\ 2L & \text{if } m = n = 0, \end{cases} \tag{11.8}$$

$$\int_{-L}^{L} \sin\left(\frac{m\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)\mathrm{d}x = \begin{cases} \delta_{mn}L & \\ 0 & \text{if } m = n = 0. \end{cases} \tag{11.9}$$

Two different functions that yield zero when multiplied together and integrated are said to be *orthogonal to each other*. This terminology is analogous to that used with vectors. Two vectors that are perpendicular to each other are also said to be orthogonal to each other. Equations (11.4), (11.5), and (11.6) indicate that all the basis functions for the Fourier series of period $2L$ are *orthogonal* to each other. An integral of the product of two functions is sometimes called a *scalar product* of the two functions.

Exercise 11.2. Sketch a rough graph of the product $\cos\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi x}{L}\right)$ from 0 to L and convince yourself that its integral from $-L$ to L vanishes.

We now show how to find the coefficients in a Fourier series. To find a_m, where $m \neq 0$ we multiply both sides of Eq. (11.1) by $\cos(m\pi x/L)$ and integrate from $-L$ to L.

$$\int_{-L}^{L} f(x)\cos\left(\frac{m\pi x}{L}\right)\mathrm{d}x = \sum_{n=0}^{\infty} a_n \int_{-L}^{L} \cos\left(\frac{n\pi x}{L}\right)\cos\left(\frac{m\pi x}{L}\right)\mathrm{d}x + \sum_{n=1}^{\infty} b_n \int_{-L}^{L} \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{m\pi x}{L}\right)\mathrm{d}x. \tag{11.10}$$

We have incorporated the a_0 term into the first sum, using the fact that $\cos(0) = 1$ and have deleted the $n = 0$ term from the second sum because $\sin(0) = 0$. We have also used the fact that the integral of a sum is equal to the sum of the integrals of the terms if the series is uniformly convergent.

We now apply the orthogonality facts, Eqs. (11.4)–(11.6), to find that all of the integrals on the right-hand side of Eq. (11.10) vanish except for the term with two cosines in which $n = m$. The result is

$$\int_{-L}^{L} f(x)\cos\left(\frac{m\pi x}{L}\right)\mathrm{d}x = a_m L. \tag{11.11}$$

This is a formula for finding all of the a coefficients except for a_0. To find a_0, we use the fact that

$$\int_{-L}^{L} \cos(0)\cos(0)\mathrm{d}x = \int_{-L}^{L} \mathrm{d}x = 2L. \tag{11.12}$$

We can now write our working equations for the a coefficients:

$$\boxed{a_0 = \frac{1}{2L}\int_{-L}^{L} f(x)\mathrm{d}x}, \tag{11.13}$$

$$\boxed{a_n = \frac{1}{L}\int_{-L}^{L} f(x)\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x \ (n \neq 0)}. \tag{11.14}$$

A similar procedure consisting of multiplication by $\sin(m\pi x/L)$and integration from $-L$ to L yields

$$\boxed{b_n = \frac{1}{L}\int_{-L}^{L} f(x)\sin\left(\frac{n\pi x}{L}\right)\mathrm{d}x}. \tag{11.15}$$

Exercise 11.3. Show that Eq. (11.15) is correct.

A function does not have to be analytic, or even continuous, in order to be represented by a Fourier series. It is only necessary that the function be integrable. An integrable function can have step discontinuities, as long as the step in the function is finite. At a step discontinuity, a Fourier series will converge to a value halfway between the value just to the right of the discontinuity and the value just to the left of the discontinuity.

We can represent a function that is not necessarily periodic by a Fourier series if we are only interested in representing the function in the interval $-L < x < L$. The Fourier series will be periodic with period $2L$, and the series will be equal to the function inside the interval, but not necessarily equal to the function outside the interval.

If the function $f(x)$ is an even function, all of the b_n coefficients will vanish, and only the cosine terms will appear in the series. Such a series is called a *Fourier cosine series*. If $f(x)$ is an odd function, only the sine terms will

appear, and the series is called a *Fourier sine series*. If we want to represent a function only in the interval $0 < x < L$, we can regard it as the right half of an odd function or the right half of an even function, and can therefore represent it either with a sine series or a cosine series. These two series would have the same value in the interval $0 < x < L$ but would be the negatives of each other in the interval $-L < x < 0$.

Example 11.1. Find the Fourier series to represent the function $f(x) = x$ for the interval $-L < x < L$. The function is represented in Figure 11.1.

The function is odd in the interval $(-L, L)$ so the series will be a sine series. Although we defined the function only for the interval $(-L, L)$, the series will be periodic and will represent the "sawtooth" function that is shown in Figure 11.1.

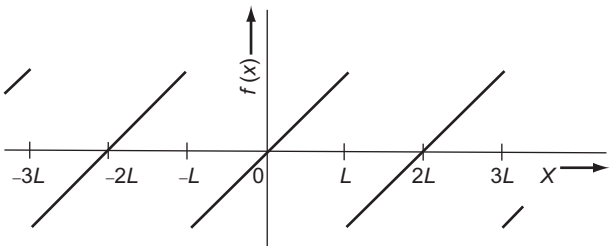


FIGURE 11.1 The sawtooth function.

The coefficients are obtained from Eq. (11.15). Since the integrand is the product of two odd functions, it is an even function and the integral is equal to twice the integral from 0 to L:

$$u = \frac{n\pi x}{L},$$

$$\begin{aligned} b_n &= \frac{2}{L} x \sin\left(\frac{n\pi x}{L}\right) \mathrm{d}x = \frac{2}{L}\left(\frac{L}{n\pi}\right)^2 \int_0^{n\pi} u \sin(u) \mathrm{d}u \\ &= \frac{2L}{(n\pi)^2}[\sin(u) - u\cos(u)]\Big|_0^{n\pi} \\ &= \frac{2L}{(n\pi)^2}[\sin(n\pi) - n\pi\cos(n\pi) - 0] \\ &= \frac{2L}{(n\pi)^2}[-n\pi\cos(n\pi)] = \frac{2L}{n\pi}(-1)^{n-1}. \end{aligned}$$

The series is

$$f(x) = \sum_{n-1}^{\infty} \frac{2L}{n\pi}(-1)^{n-1} \sin\left(\frac{n\pi x}{L}\right).$$

Exercise 11.4. Show that the a_n coefficients for the series representing the function in the previous example all vanish.

Example 11.2. Show that the series of the previous example equals zero at $x = -L$, $x = L$, and $x = 3L$, the value halfway between the two values of the function at the step discontinuity.

We begin with $x = L$

$$\sin\left(\frac{n\pi L}{L}\right) = \sin(n\pi) = 0.$$

Since all of the sine functions vanish, the series vanishes. For $x = -L$ and $x = 3L$, and so on, the sine functions also vanish and the series vanishes.

Exercise 11.5. Find the Fourier cosine series for the even function

$$f(x) = |x| \quad \text{for} - L < x < L.$$

Sketch a graph of the periodic function that is represented by the series.

It is a necessary condition for the convergence of Fourier series that the coefficients become smaller and smaller and approach zero as n becomes larger and larger. If convergence is fairly rapid, it might be possible to approximate a Fourier series by a partial sum. Figure 11.2 shows three different partial sums of the Fourier sine series that represents the "square-wave" function

$$f(x) = \begin{cases} +1 & \text{for } 0 < x < L, \\ -1 & \text{for } -L < x < 0. \end{cases} \tag{11.16}$$

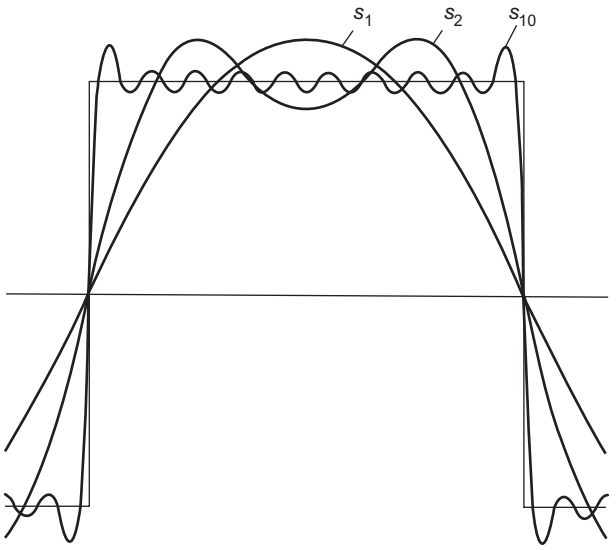


FIGURE 11.2 The square wave function approximated by S_1, S_2, and S_{10}.

Only the right half of one period is shown. The first partial sum only vaguely resembles the function, but S_{10} is a better approximation. Notice the little spike or overshoot near the discontinuity. This is a typical behavior and is known as the *Gibbs phenomenon*.[3] The partial sum S_{100} fits the function

[3] Named for Josiah Willard Gibbs, 1839–1903, a prominent American physicist who made important contributions to mathematics and chemistry as well as to physics.

more closely away from the discontinuity, but it has a spike near the discontinuity that is just as high as that of S_{10}, although much narrower.

11.1.2 Fourier Series with Complex Exponential Basis Functions

The sine and cosine basis functions are closely related to complex exponential functions, as shown by the identities

$$\cos(\alpha) = \frac{1}{2}\left(e^{i\alpha} + e^{-i\alpha}\right), \tag{11.17}$$

$$\sin(\alpha) = \frac{1}{2i}\left(e^{i\alpha} - e^{-i\alpha}\right). \tag{11.18}$$

One can write

$$a_n \cos\left(\frac{n\pi x}{L}\right) + b_n \sin\left(\frac{n\pi x}{L}\right) = \frac{1}{2}(a_n + ib_n)e^{in\pi x/L} + \frac{1}{2}(a_n - ib_n)e^{-in\pi x/L}. \tag{11.19}$$

It is therefore possible to rewrite Eq. (11.1) as an exponential Fourier series:

$$\boxed{f(x) = \sum_{n=-\infty}^{\infty} c_n e^{in\pi x/L} = \sum_{n=-\infty}^{\infty} c_n \exp\left(\tfrac{in\pi x}{L}\right)}. \tag{11.20}$$

We have incorporated the terms with negative exponents into the same sum with the other terms by allowing the summation index to take on negative as well as positive values. A Fourier series does not have to represent a real function and the coefficients do not have to be real. If we represent a real function, the coefficients a_n and b_n will be real and the coefficients c_n will be complex. The orthogonality of the complex exponentials is a little different from the orthogonality of the sine and cosine functions, in that the complex conjugate of one of the functions must be taken before integration.

$$\int_{-L}^{L} \left[\exp\left(\frac{im\pi x}{L}\right)\right]^* \exp\left(\frac{in\pi x}{L}\right) \mathrm{d}x = \int_{-L}^{L} \exp\left(\frac{-im\pi x}{L}\right) \exp\left(\frac{in\pi x}{L}\right) \mathrm{d}x = 2L\delta_{mn}. \tag{11.21}$$

Exercise 11.6. Derive the orthogonality relation expressed above.

The coefficient c_n is obtained by multiplying by $\exp\left(-im\pi x/L\right)$ and integrating:

$$\int_{-L}^{L} \exp\left(\frac{-im\pi x}{L}\right) f(x)\mathrm{d}x = \int_{-L}^{L} \sum_{n=-\infty}^{\infty} c_n \exp\left(\frac{-im\pi x}{L}\right) \exp\left(\frac{in\pi x}{L}\right) \mathrm{d}x. \tag{11.22}$$

The sum and the integral are uniformly convergent so we can interchange the order of summing and integrating:

$$\int_{-L}^{L} \exp\left(\frac{-im\pi x}{L}\right) f(x)\mathrm{d}x = \sum_{n=-\infty}^{\infty} c_n \int_{-L}^{L} \exp\left(\frac{-im\pi x}{L}\right) \times \exp\left(\frac{in\pi x}{L}\right) \mathrm{d}x \tag{11.23}$$

$$= \sum_{n=-\infty}^{\infty} c_n 2L\delta_{mn} = 2Lc_m. \tag{11.24}$$

The last equality comes from the fact that all of the terms in the sum vanish except for the term with $m = n$. We now have

$$c_m = \frac{1}{2L}\int_{-L}^{L} \exp\left(\frac{-im\pi x}{L}\right) f(x)\mathrm{d}x. \tag{11.25}$$

11.2 OTHER FUNCTIONAL SERIES WITH ORTHOGONAL BASIS SETS

Fourier series are just one example of series using orthogonal sets of basis functions. In quantum mechanics it is found that certain sets of wave functions form orthogonal sets of functions, and these can be used as basis functions. It is generally assumed that such a set of functions is complete for representation of functions that obey the same boundary conditions as the basis functions. For example, if the basis functions vanish at $x = \pm\infty$ or at some other points, the function to be represented must vanish at the same points. Assume that we have a complete set of orthogonal basis functions, called $\psi_1, \psi_2, \psi_3, \ldots, \psi_n \ldots$, that depend on the independent variable x. Since the set of functions is assumed to be complete, we can expand an arbitrary function, f, in terms of the ψ functions so long as f obeys the same boundary conditions as the ψ functions:

$$f = \sum_n c_n \psi_n, \tag{11.26}$$

where the expansion coefficients $c_1, c_2, c_3, \ldots, c_n, \ldots$ are to be determined.

11.2.1 Hilbert Space

Equation (11.26) is analogous to the representation of a vector in terms of its three components:

$$\mathbf{A} = \mathbf{i}A_x + \mathbf{j}A_y + \mathbf{k}A_z. \tag{11.27}$$

The function f in Eq. (11.26) plays the same role as the vector $\mathbf{A}$, the basis functions $\psi_1, \psi_2, \ldots$ play the same role as the unit vectors, and the expansion coefficients $c_1, c_2, \ldots$ play the same role as the components A_x, A_y, and A_z. Instead of summing over three unit vectors, we sum over all of the basis functions in the complete set. Mathematicians have defined a hypothetical mathematical space called *Hilbert space* in order to exploit the analogy between basis functions and unit vectors in ordinary space. In Hilbert space, there is a "dimension" for each basis function, just as in ordinary space there is a dimension for each unit vector. We sometimes say that the unit vectors **i**, **j**, and **k** *span* the three-dimensional physical space, and we say that the basis functions $\psi_1, \psi_2, \psi_3, \ldots, \psi_n, \ldots$ span the Hilbert space, which has as many dimensions as there are basis functions.

In order to complete the analogy between physical space and Hilbert space, we define the scalar product of two functions, $f(x)$ and $g(x)$, by

$$\text{scalar product of } f(x) \text{ and } g(x) = \int f^*(x) g(x) \mathrm{d}x. \tag{11.28}$$

If the functions are complex, the complex conjugate of the first factor must be taken. If the functions depend on x, y, and z, the scalar product is

$$\text{scalar product of } f(x,y,z) \text{ and } g(x,y,z) = \iiint f^*(x,y,z) g(x,y,z) \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z, \tag{11.29}$$

where the integration is over all possible values of the variables on which the functions depend. If the limits of integration are infinite, this integral must converge.

We assume that the basis functions are *normalized* and *orthogonal* to each other. This means that the functions have been multiplied by appropriate constants so that the scalar product of any one of the functions with itself equals unity and that the scalar product of two different functions vanishes.

$$\int \psi_n^* \psi_m \, \mathrm{d}x = \delta_{nm} = \begin{cases} 1 & \text{if } n = m, \\ 0 & \text{if } n \neq m. \end{cases} \tag{11.30}$$

This equation is completely analogous to the normalization and orthogonality of the unit vectors:

$$\begin{aligned} &\mathbf{i} \cdot \mathbf{i} = \mathbf{j} \cdot \mathbf{j} = \mathbf{k} \cdot \mathbf{k} = \mathbf{1}, \\ &\mathbf{i} \cdot \mathbf{j} = \mathbf{j} \cdot \mathbf{k} = \mathbf{k} \cdot \mathbf{i} = \mathbf{0}. \end{aligned} \tag{11.31}$$

You can think of the basis functions as being perpendicular to each other in the hypothetical Hilbert space, and you can think of the expansion coefficients as components in the respective directions in Hilbert space.

11.2.2 Determining the Expansion Coefficients

In order to find the c coefficients in Eq. (11.26), we multiply by the complex conjugate of ψ_m and integrate:

$$\boxed{\int \psi_m^* f \, \mathrm{d}x = \sum_n c_n \int \psi_m^* \psi_n \mathrm{d}x = \sum_n c_n \delta_{nm} = c_m}. \tag{11.32}$$

When the final sum over n is carried out, only the $n = m$ term survives because of the orthogonality of the basis functions. Equations (11.13), (11.14), and (11.15) are special cases of this equation.

Example 11.3. The normalized quantum-mechanical wave functions for the particle in a one-dimensional box of length a are

$$\psi_n = \left(\frac{2}{a}\right)^{1/2} \sin(n\pi x/a).$$

These functions are a complete set for expansion of functions that are defined in the region $0 < x < a$ and vanish at $x = 0$ and at $x = a$. Find the coefficient c_1 if $f = x^2 - ax$.

$$\begin{aligned} c_1 &= \left(\frac{2}{a}\right)^{1/2} \left(\int_0^a x^2 \sin(\pi x/a) \mathrm{d}x \right. \\ &\qquad \left. -a \int_0^a x \sin(\pi x/a) \mathrm{d}x \right) \\ &= \left(\frac{2}{a}\right)^{1/2} \left(\frac{a}{\pi}\right)^3 \int_0^\pi y^2 \sin(y) \mathrm{d}y \\ &\quad -a \left(\frac{2}{a}\right)^{1/2} \left(\frac{a}{\pi}\right)^2 \int_0^\pi y \sin(y) \mathrm{d}y \\ &= \left(\frac{2}{a}\right)^{1/2} \left(\frac{a}{\pi}\right)^3 \left[2y \sin(y) - (y^2 - 2)\cos(y)\right] \Big|_0^\pi \\ &\quad -a \left(\frac{2}{a}\right)^{1/2} \left(\frac{a}{\pi}\right)^2 \left[\sin(y) - y\cos(y)\right] \Big|_0^\pi \\ &= \left(\frac{2}{a}\right)^{1/2} \left(\frac{a}{\pi}\right)^3 \left[0 - (\pi^2 - 2)(-1) - 0 + (-2)(1)\right] \\ &\quad -a \left(\frac{2}{a}\right)^{1/2} \left(\frac{a}{\pi}\right)^2 \left[0 - \pi(-1) - 0\right] \\ &= -\frac{4\sqrt{2}a^{5/2}}{\pi^3} = -0.182442 a^{5/2}. \end{aligned}$$

This corresponds to

$$\begin{aligned} f &= x^2 - ax \approx -\frac{4\sqrt{2}a^{5/2}}{\pi^3} \left(\frac{2}{a}\right)^{1/2} \sin(\pi x/a) \\ &\approx -\frac{8a^2}{\pi^3} \sin(\pi x/a) = -0.258012 a^2 \sin(\pi x/a). \end{aligned}$$

This is one term of a Fourier series.

Exercise 11.7. Construct a graph with the function f from the previous example and $c_1\psi_1$ on the same graph. Let $a = 1$ for your graph. Comment on how well the partial sum with one term approximates the function.

11.3 INTEGRAL TRANSFORMS

Integral transforms are closely related to functional series. However, instead of a sum with each term consisting of a coefficient multiplying a basis function, we have an integral in which the summation index is replaced by an integration variable. The basis functions are multiplied by a function of this integration variable, and integration over this variable yields a representation of the function. This function is called the *integral transform* of the given function and is analogous to the set of expansion coefficients. There are several kinds of integral transforms, including Mellin transforms, Hankel transforms, and so forth,[4] but the principal transforms encountered by physical chemists are Fourier transforms and Laplace transforms.

11.3.1 Fourier Transforms (Fourier Integrals)

The Fourier series using complex exponential basis functions is

$$f(x) = \sum_{n=-\infty}^{\infty} c_n e^{in\pi x/L} = \sum_{n=-\infty}^{\infty} c_n \exp\left(\frac{in\pi x}{L}\right). \tag{11.33}$$

If we allow L to become larger and larger, the values of $n\pi x/L$ become closer and closer together. We let

$$k = \frac{n\pi}{L}. \tag{11.34}$$

As the limit $L \to \infty$ is taken, k becomes a continuously variable quantity. In this limit, the exponential Fourier series becomes an integral, which is called a *Fourier integral* or a *Fourier transform*,

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k) e^{ikx}\, \mathrm{d}k, \tag{11.35}$$

where the coefficient c_n in Eq. (11.20) is replaced by a function of k, denoted by $F(k)$ and the sum over n is replaced by an integral over k. The function $f(x)$ is no longer required to be a periodic function and the Fourier integral can represent the function for all values of x.

The equation for determining $F(k)$ is analogous to Eqs. (11.13–11.15)

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx}\, \mathrm{d}x. \tag{11.36}$$

[4] A. Erdelyi Ed., *Tables of Integral Transforms*, Vols. I and II, McGraw–Hill, New York, 1954; A. G. Marshall. Ed., *Fourier, Hadamard, and Hilbert Transforms in Chemistry*, Plenum, New York, 1982.

We have introduced a factor of $1\sqrt{2\pi}$ in front of the integral in Eq. (11.35) in order to have the same factor in front of this integral and the integral in Eq. (11.36). Note that the factor e^{ikx} occurs in the integral for $f(z)$, while the factor e^{-ikx} occurs in the integral for $F(k)$. The function $F(k)$ is called the *Fourier transform* of $f(x)$ and the function $f(x)$ is also called the *Fourier transform* of $F(k)$. For the integral in Eq. (11.35) to converge, the following integral must converge:

$$\int_{-\infty}^{\infty} |f(x)|^2 \mathrm{d}x \prec \infty. \tag{11.37}$$

We say that the function $f(x)$ must be *square integrable* which implies that the function $f(x)$ must approach zero as $|x| \to \infty$. If the Fourier transform $F(k)$ exists, it will also be square integrable.

The Gaussian function occurs prominently in probability theory and is given by the formula

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right], \tag{11.38}$$

where μ is the mean value of the variable x and σ is the standard deviation. The standard deviation is a measure of the width of the distribution described by the function. Figure 11.3 shows a Gaussian function.

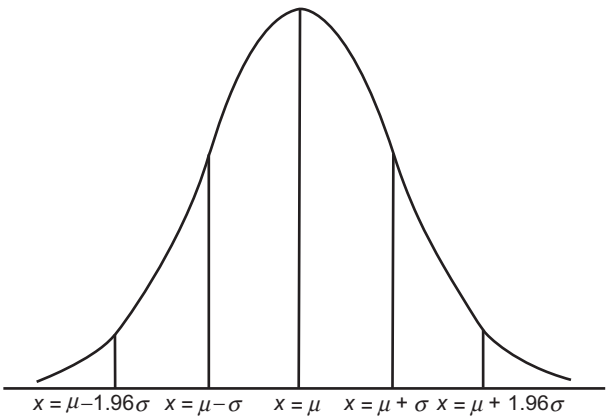


FIGURE 11.3 The Gaussian function.

Example 11.4. Find the Fourier transform of the Gaussian function

$$f(x) = e^{-ax^2},$$

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ax^2} e^{-ikx}\, \mathrm{d}x,$$

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ax^2} \cos(kx)\mathrm{d}x - \frac{i}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ax^2} \sin(kx)\mathrm{d}x.$$

The first integral is twice the integral of Eq. (37) of Appendix F, and the second integral vanishes since the integrand is an odd function.

$$F(k) = \frac{2}{\sqrt{2\pi}} \int_{0}^{\infty} e^{-ax^2} \cos(kx)\mathrm{d}x = \frac{2}{\sqrt{2\pi}} \frac{1}{2} \sqrt{\frac{\pi}{a}} e^{-k^2/4a} = \frac{1}{\sqrt{2a}} e^{-k^2/4a}.$$

This version of the transform is called a one-sided cosine transform.

The Fourier transform of a Gaussian function of x is a Gaussian function of k. The standard deviation of $f(x)$ is inversely proportional to the standard deviation of $F(k)$.

If the function $f(x)$ is an even function, its Fourier transform can be a *Fourier cosine transform*:

$$F(k) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} f(x) \cos(kx)\mathrm{d}x = \sqrt{\frac{2}{\pi}} \int_{0}^{\infty} f(x) \cos(kx)\mathrm{d}x \quad (f \text{ even}). \tag{11.39}$$

If $f(x)$ is an odd function, its Fourier transform is a *Fourier sine transform*:

$$F(k) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} f(x) \sin(kx)\mathrm{d}x = \sqrt{\frac{2}{\pi}} \int_{0}^{\infty} f(x) \sin(kx)\mathrm{d}x \quad (f \text{ odd}). \tag{11.40}$$

Exercise 11.8. Find the Fourier transform of the function $f(x) = e^{-|t|}$. Since this is an even function, you can use the one-sided cosine transform.

Fourier transforms are frequently used to represent functions of time, and one-sided transforms can be used if negative times are not included:

$$f(t) = \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} F(\omega) e^{i\omega t}\, \mathrm{d}\omega, \tag{11.41}$$

$$F(\omega) = \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} f(t) e^{-i\omega t}\, \mathrm{d}t. \tag{11.42}$$

We can think of the factor $e^{i\omega t}$ as representing an oscillating wave and can think of the function $f(t)$ as representing a collection of waves of different frequencies that interfere constructively and destructively. The quantity $F(\omega)$ represents the relative intensity of the wave as a function of the *circular frequency*, ω, which relates to the frequency of the wave, ν, by

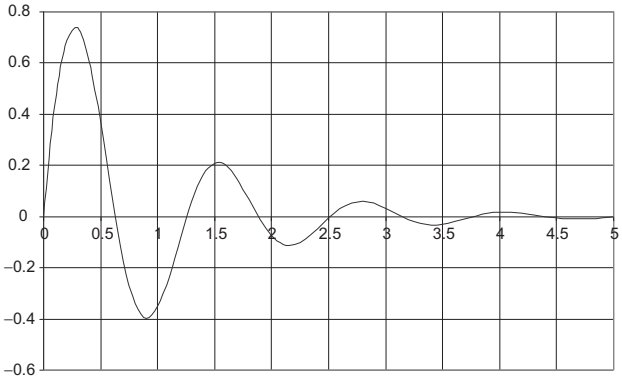
$$\omega = 2\pi\nu. \tag{11.43}$$

The principal uses of Fourier transforms in physical chemistry are in spectroscopy. Modern infrared spectrometers and NMR spectrometers use Fourier transforms. A signal is produced as a function of time, and a Fourier transform is performed to obtain a function of frequency, which represents the spectrum. In an infrared spectrometer, an interferogram signal is obtained and its Fourier transform represents the spectrum. In a Fourier-transform NMR apparatus, a signal called a "free-induction decay" (FID) signal is detected and fed into a computer where a Fourier transform is performed numerically. The result is the spectrum in terms of the circular frequency. Since the Fourier transform must be performed for many different values of the frequency, the procedure is made possible by an algorithm known as a "fast Fourier transform," abbreviated as FFT. If a single NMR frequency is involved, the FID signal is a ringing exponential function, as in the following example.

Example 11.5. Find the one-sided sine transform of the "ringing exponential" function

$$f = e^{-at} \sin(bt).$$

This function resembles a free-induction decay (FID) signal from a Fourier-transform NMR instrument and is depicted in the following graph for the case that $a = 1.00\ \mathrm{s}^{-1}$ and $b = 5.00\ \mathrm{s}^{-1}$.



The transform is given by the integral

$$F(\omega) = \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} e^{-at} \sin(bt) \sin(\omega t)\mathrm{d}t.$$

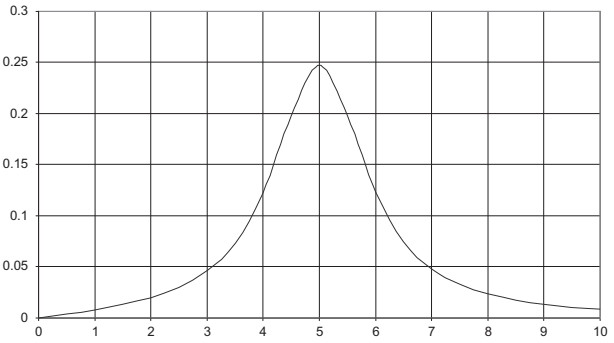
This integral is found in Appendix G:

$$F(\omega) = \frac{2}{\sqrt{\pi}} \frac{2ab\omega}{[a^2 + (b-\omega)^2][a^2 + (b+\omega)^2]}.$$

With $a = 1.00\ \text{s}^{-1}$ and $b = 10.0\ \text{s}^{-1}$, we have

$$F(\omega) = \frac{2}{\sqrt{\pi}} \frac{(10.00\ \text{s}^{-2})\omega}{[1.00\ \text{s}^{-2} + (10.00\ \text{s}^{-1} - \omega)^2][1.00\ \text{s}^{-2} + (10.00\ \text{s}^{-1} + \omega)^2]}.$$

The following graph shows the function $F(\omega)$. We have ignored a constant factor for this graph. This curve resembles an NMR absorption line.



Exercise 11.9. Repeat the calculation of the previous example with $a = 0.500\ \text{s}^{-1}$. Show that a narrower line width occurs.

If two resonant frequencies are involved, the FID signal could be a sum of two ringing exponentials:

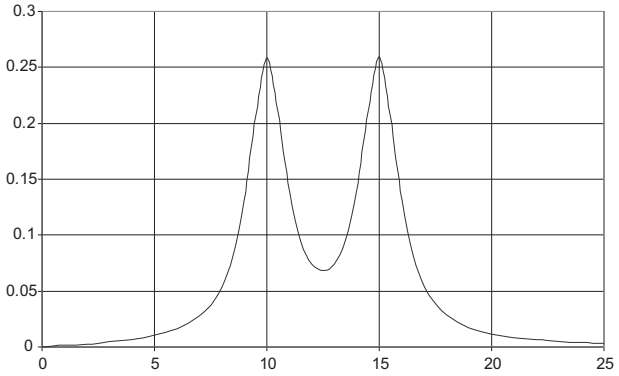
$$f(t) = e^{-at} \sin(bt) + e^{-at} \sin(ct).$$

Example 11.6. Find the Fourier transform of the following function, which is a sum of two ringing exponentials, with $a = 1.00\ \text{s}^{-1}$, $b = 10.00\ \text{s}^{-1}$, $c = 15.00\ \text{s}^{-1}$:

$$f(t) = e^{-(1.00\ \text{s}^{-1})t} \sin[(10.00\ \text{s}^{-1})t] + e^{-(1.00\ \text{s}^{-1})t} \sin[(15.00\ \text{s}^{-1})t],$$

$$F(\omega) = \frac{2}{\sqrt{\pi}} \frac{2ab\omega}{[a^2 + (b-\omega)^2][a^2 + (b+\omega)^2]} + \frac{2}{\sqrt{\pi}} \frac{2ac\omega}{[a^2 + (c-\omega)^2][a^2 + (c+\omega)^2]} = \frac{2}{\sqrt{\pi}} \times \frac{2(10.00\ \text{s}^{-2})\omega}{[(1.00\ \text{s}^{-1})^2 + (10.00\ \text{s}^{-1} - \omega)^2][(1.00\ \text{s}^{-1})^2 + (10.00\ \text{s}^{-1} + \omega)^2]} + \frac{2}{\sqrt{\pi}} \times \frac{2(15.00\ \text{s}^{-2})\omega}{[(1.00\ \text{s}^{-1})^2 + (15.00\ \text{s}^{-1} - \omega)^2][(1.00\ \text{s}^{-1})^2 + (15.00\ \text{s}^{-1} + \omega)^2]}.$$

The following graph shows a graph of this function, omitting a constant factor. This curve resembles two lines with different chemical shifts in an NMR spectrum.



11.3.2 Laplace Transforms

The *Laplace transform*[5] $F(s)$ of the function $f(t)$ is defined by

$$\boxed{F(s) = \int_0^\infty f(t) e^{-st} \mathrm{d}t} \quad \text{(definition)}. \tag{11.44}$$

As with the Fourier transform, we denote a Laplace transform by a capital letter and the function by a lowercase letter. The Laplace transform is similar to a one-sided Fourier transform, except that it has a real exponential instead of the complex exponential of the Fourier transform. If we consider complex values of the variables, the two transforms become different versions of the same transform, and their properties are related.[6] The integral that is carried out to invert the Laplace transform must be carried out in the complex plane, and we do not discuss it. Fortunately, it is often possible to apply Laplace transforms without carrying out such an integral by applying some useful theorems.[7] We will discuss the use of Laplace transforms in solving differential equations in Chapter 12.

The Laplace transform and its inverse are often denoted in the following way:

$$F(s) = \mathcal{L}\{f(t)\}, \tag{11.45}$$

$$f(t) = \mathcal{L}^{-1}\{F(s)\}. \tag{11.46}$$

Table 11.1 gives a few common Laplace transforms.[8]

Example 11.7. Find the Laplace transform of the function $f(t) = t^2$.

$$F(s) = \int_0^\infty t^2 e^{-st}\, \mathrm{d}t = \frac{1}{s^3} \int_0^\infty u^2\, e^{-u}\, \mathrm{d}u = \frac{2!}{s^3} = \frac{2}{s^3},$$

where we have used Eq. (1) of Appendix F.

[5] The Laplace transform is named for Pierre Simon Laplace, Marquis de LaPlace, 1749–1827, French astronomer and mathematician.
[6] Philip M. Morse and Herman Feshbach, op. cit., pp. 467ff.
[7] Erwin Kreyszig, *Advanced Engineering Mathematics*, 3rd ed., pp. 147ff, Wiley, New York, 1972.
[8] Erwin Kreyszig, *Advanced Engineering Mathematics*, 3rd ed., Wiley, New York, 1962, p. 149.

TABLE 11.1 Some Common Laplace Transforms

$F(s)$	$f(t)$
$1/s$	1
$1/s^2$	t
$n!/s^{n+1}$	t^n
$\frac{\Gamma(a+1)_9}{s^{a+1}}$	$t^a (a \succ 0)$
$\frac{1}{s-a}$	$e^{at} (s \succ a)$
$\frac{s}{s^2+a^2}$	$\cos(at)$
$\frac{a}{s^2+a^2}$	$\sin(at)$
$\frac{s}{s^2-a^2}$	$\cosh(at)$
$\frac{a}{s^2-a^2}$	$\sinh(at)$

Exercise 11.10. Find the Laplace transform of the function $f(t) = e^{at}$ where a is a constant.

There are several theorems pertaining to Laplace transforms, and we present a few of them without proofs.[9]

The *shifting theorem* implies:

$$\boxed{\mathcal{L}\{e^{at} f(t)\} = F(s-a)}. \tag{11.47}$$

The *derivative theorem* implies:

$$\boxed{\mathcal{L}\left\{\frac{\mathrm{d}f}{\mathrm{d}t}\right\} = \mathcal{L}\{f^{(1)}(t)\} = s\mathcal{L}\{f(t)\} - f(0)}, \tag{11.48}$$

where we use the notation $f^{(1)}$ for the first derivative of f, $f^{(2)}$for the second derivative of f, and so on.

The derivative theorem can be applied repeatedly to obtain the extended version of the derivative theorem,

$$\boxed{\mathcal{L}\{f^{(n)}\} = s^n\mathcal{L}\{f\} - s^{n-1}f(0) - s^{n-2}f^{(1)}(0) - \cdots - f^{(n-1)}(0)}. \tag{11.49}$$

Exercise 11.11. Derive the version of Eq. (11.49) for $n = 2$.

The *integral theorem* implies :

$$\boxed{\mathcal{L}\left\{\int_0^t f(u)\mathrm{d}u\right\} = \tfrac{1}{s}\mathcal{L}\{f(t)\}}. \tag{11.50}$$

These theorems can be used to obtain Laplace transforms from Laplace transforms of other functions.

[9] Erwin Kreyszig, Advanced Engineering Mathematics, 8th ed., Wiley, New York, 1999.

Example 11.8. Use the shifting theorem to obtain the Laplace transform of the function

$$f(t) = e^{at}\cos(kt).$$

We transcribe the entry for $\cos(kx)$ from Table 11.1, replacing s by $s - a$, obtaining

$$F(s) = \frac{s-a}{(s-a)^2 + k^2.}$$

Exercise 11.12. Find the Laplace transform of the function

$$f(t) = t^n e^{at},$$

where n is an integer.

Example 11.9. Find the inverse Laplace transform of

$$\frac{1}{s(s-a)}.$$

From Table 11.1, we recognize $1/(s-a)$ as the Laplace transform of e^{at}. From the integral theorem,

$$\mathcal{L}\left\{\int_0^t e^{au}\,\mathrm{d}u\right\} = \frac{1}{s}\mathcal{L}\{e^{at}\} = \frac{1}{s}\frac{1}{s-a}.$$

Therefore, the inverse transform is

$$\mathcal{L}^{-1}\left\{\frac{1}{s(s-a)}\right\} = \int_0^t e^{au}\,\mathrm{d}u = \frac{1}{a}(e^{at} - 1).$$

Exercise 11.13. Find the inverse Laplace transform of

$$\frac{1}{s(s^2+k^2)}.$$

PROBLEMS

1. Find the Fourier series that represents the square wave

$$A(t) = \begin{cases} -A_0 & -T < t < 0, \\ A_0 & 0 < t < T, \end{cases}$$

where A_0 is a constant and $T$is the period. Make graphs of the first two partial sums.

2. Find the Fourier series to represent the function

$$f(x) = \begin{cases} -1 \text{ if } -L \prec x \prec -L/2, \\ \ \ 1 \text{ if } -L/2 \prec x \prec L/2, \\ -1 \text{ if } L/2 \prec x \prec L. \end{cases}$$

Construct a graph showing the first three terms of the series and the third partial sums.

3. Find the Fourier series to represent the function

$$A(t) = \begin{cases} e^{-|x|} & -L < t < L, \\ 0 & \text{elsewhere.} \end{cases}$$

Your series will be periodic and will represent the function only in the region $-L < t < L$.

4. Find the one-sided Fourier cosine transform of the function $f(x) = xe^{-ax}$.

5. Find the one-sided Fourier sine transform of the function $f(x) = \frac{e^{-ax}}{x}$.

6. Find the Fourier transform of the function $\exp(-(x - x_0)^2)$.

7. Find the one-sided Fourier sine transform of the function ae^{-bx}.

8. Find the one-sided Fourier cosine transform of the function $a/(b^2 + t^2)$.

9. Find the one-sided Fourier sine transform of the function $f(x) = x$.

10. Show that $\mathcal{L}\{t \cos(kt)\} = (s^2 - k^2)/(s^2 + k^2)^2$.

11. Find the Laplace transform of $\cos^2(at)$.

12. Find the Laplace transform of $\sin^2(at)$.

13. Use the derivative theorem to derive the Laplace transform of $\cos(at)$ from the Laplace transform of $\sin(at)$.

14. Find the inverse Laplace transform of $1/(s^2 - a^2)$.

Chapter 12

Differential Equations

Principal Facts and Ideas

- The solution of a differential equation is a function whose derivative or derivatives satisfy the equation.
- An equation of motion is a differential equation obtained from Newton's second law of motion, $\mathbf{F} = m\mathbf{a}$.
- In principle, an equation of motion can be solved to give the position and velocity as a function of time for every particle in a system governed by Newton's laws of motion.
- Some differential equations can be solved by separation of variables.
- A homogeneous linear differential equation with constant coefficients can be solved by use of an exponential trial solution.
- An inhomogeneous linear differential equation can be solved if a particular solution can be found.
- An exact differential equation can be solved by a line integration.
- Some inexact differential equations can be converted to exact differential equations by multiplication by an integrating factor.
- Some partial differential equations can be solved by separation of variables.
- Some differential equations can be transformed into algebraic equations by a Laplace transformation. Solution of this equation followed by inverse transformation provides a solution to the differential equation.
- Differential equations can be solved numerically by a variety of methods, including the use of Mathematica.

Objectives

After studying this chapter, you should be able to:

- construct an equation of motion for a particle from Newton's second law;
- solve a linear homogeneous differential equation with constant coefficients;
- solve a differential equation whose variables can be separated;
- solve an exact differential equation;
- use an integrating factor to solve an inexact differential equation;
- solve a simple partial differential equation by separation of variables;
- solve a differential equation by use of Laplace transforms;
- use Mathematica to solve differential equations symbolically and numerically.

12.1 DIFFERENTIAL EQUATIONS AND NEWTON'S LAWS OF MOTION

A *differential equation* is an equation that contains one or more derivations of an unknown function. The solution of a differential equation is a function that satisfies the equation. Our first examples of differential equations are classical *equations of motion*, which involve the position, velocity, and acceleration of particles. The position of a particle is given by the *position vector* $\mathbf{r}$ with Cartesian components x, y, and z:

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z, \tag{12.1}$$

where $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are the unit vectors defined in Chapter 4. The *velocity* $\mathbf{v}$ of a particle is the rate of change of its position vector,

$$\mathbf{v} = \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = \mathbf{i}\frac{\mathrm{d}x}{\mathrm{d}t} + \mathbf{j}\frac{\mathrm{d}y}{\mathrm{d}t} + \mathbf{k}\frac{\mathrm{d}z}{\mathrm{d}t} = \mathbf{i}v_x + \mathbf{j}v_y + \mathbf{k}v_z. \tag{12.2}$$

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00012-4

The *acceleration* **a** is the rate of change of the velocity:

$$\mathbf{a} = \mathbf{i}a_x + \mathbf{j}a_y + \mathbf{k}a_z = \frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = \frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} = \mathbf{i}\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + \mathbf{j}\frac{\mathrm{d}^2y}{\mathrm{d}t^2} + \mathbf{k}\frac{\mathrm{d}^2z}{\mathrm{d}t^2}. \tag{12.3}$$

Equations of motion are obtained from Newton's three laws of motion: [1]

1. A body on which no forces act does not accelerate.
2. A body acted on by a force **F** accelerates according to

$$\mathbf{F} = m\mathbf{a}, \tag{12.4}$$

where m is the mass of the object and **a** is its acceleration.
3. Two bodies exert forces of equal magnitude and opposite direction on each other.

Classical mechanics (sometimes called *Newtonian mechanics*) is primarily the study of the consequences of Newton's laws. We now accept them as approximations to reality that are accurate for large objects moving at speeds much less than the speed of light. The first law is just a special case of the second, and the third law is primarily used to obtain forces for the second law, so Newton's second law is the most important equation of classical mechanics.

We can write an *equation of motion* if the acceleration of a particle is known as a function of time. If the particle moves only in the z direction:

$$a_z = a_z(t). \tag{12.5}$$

We equate the time derivative of the velocity to this known function and obtain an equation of motion:

$$\frac{\mathrm{d}v_z}{\mathrm{d}t} = a_z(t). \tag{12.6}$$

To solve Eq. (12.6), we multiply both sides by $\mathrm{d}t$ and perform a definite integration from $t = 0$ to $t = t_1$.

$$v_z(t_1) - v_z(0) = \int_0^{t_1} \left(\frac{\mathrm{d}v_z}{\mathrm{d}t}\right) \mathrm{d}t = \int_0^{t_1} a_z(t)\mathrm{d}t. \tag{12.7}$$

The result of this integration gives v_z as a function of time, so that the position obeys a second differential equation

$$\frac{\mathrm{d}z}{\mathrm{d}t} = v_z(t). \tag{12.8}$$

A second integration gives the position as a function of time:

$$\begin{aligned} z_z(t_2) - z(0) &= \int_0^{t_2} \left(\frac{\mathrm{d}z}{\mathrm{d}t_1}\right) \mathrm{d}t_1 = \int_0^{t_2} v_z(t_1)\mathrm{d}t_1 \\ &= \int_0^{t_2} \left[v_z(0) + \int_0^{t_1} a_z(t)\mathrm{d}t\right] \mathrm{d}t_1 \\ &= \int_0^{t_2} v_z(0)\mathrm{d}t_1 + \int_0^{t_2}\int_0^{t_1} a_z(t)\mathrm{d}t\mathrm{d}t_1. \end{aligned} \tag{12.9}$$

There are inertial navigation systems used on submarines and space vehicles that measure the acceleration as a function of time and perform two numerical integrations in order to determine the position of the vehicle.

Example 12.1. At time $t = 0$, a certain particle has $z(0) = 0$ and $v_z(0) = 0$. Its acceleration is given as a function of time by

$$a_z(t) = a_0 e^{-t/b},$$

where a_0 and b are constants.

(a) Find v_z as a function of time.
The velocity is the antiderivative of the given acceleration function plus a constant v_0:

$$\begin{aligned} v_z(t) &= -a_0 b e^{-t/b} + v_0 \\ &= -a_0 b e^{-t/b} + a_0 b = a_0 b(1 - e^{-t/b}), \end{aligned}$$

since it was specified that $v_z(0) = 0$, the constant $v_0 = a_0 b$.

(b) Find z as a function of time.
The position is the antiderivative of the velocity plus a constant z_0:

$$\begin{aligned} z(t) &= a_0 b^2 e^{-t/b} + a_0 b t + z_0 \\ &= a_0 b^2 e^{-t/b} + a_0 b t - a_0 b^2, \end{aligned}$$

since it was specified that $z(0) = 0$, the constant z_0 is equal to $a_0 b^2$.

(c) Find the speed and the position of the particle at $t = 30.0$ s if $a_0 = 10.0$ m s^{-2} and if $b = 20.0$ s. At $t = 30.0$ s

$$\begin{aligned} v_z(30.0\text{ s}) &= (10.0\text{ m s}^{-2})(20.0\text{ s})(1 - e^{-1.50}) \\ &= 155\text{ m s}^{-1}, \\ z(30.0\text{ s}) &= (10.0\text{ m s}^{-2})(20.0\text{ s})^2 e^{-1.50} \\ &\quad + (200.0\text{ m s}^{-1})(30.0\text{ s}) \\ &\quad - (10.0\text{ m s}^{-2})(20.0\text{ s})^2 = 2890\text{ m}. \end{aligned}$$

(d) Find the limiting value of the speed as $t \to \infty$:

$$\lim_{t\to\infty} v_z(t) = a_0 b = 200.\text{ ms}^{-1}$$

[1] Isaac Newton (1642–1827) was a great English physicist who deduced the law of gravity and three laws of motion from mathematical analysis of observations on the motions of planets around the sun.

Exercise 12.1. An object falling in a vacuum near the surface of the earth experiences a gravitational force in the z direction given by

$$F_z = -mg,$$

where g is called the acceleration due to gravity and is equal to 9.80 m s^{-2}.[2] This corresponds to a constant acceleration

$$a_z = -g.$$

Find the expression for the position of the particle as a function of time. Find the position of the particle at time $t = 1.00$ s if its initial position is $z = 10.00$ m and its initial velocity is $v_z = 0$.

Equations of motion can also be obtained if the force on a particle is known as a function of position. We consider some of these in the next sections.

12.2 HOMOGENEOUS LINEAR DIFFERENTIAL EQUATIONS WITH CONSTANT COEFFICIENTS

An ordinary linear differential equation with constant coefficients has the properties:

1. Ordinary means that it contains no partial derivatives.
2. Linear means that it contains the function and its derivatives only to the first power.
3. Constant coefficients mean that the quantities multiplying the dependent variable and its derivatives are constants.

We first consider homogeneous equations, which means that there is no term that does not contain the function or its derivatives. The equation can be written

$$a_0 y + a_1 \frac{dy}{dx} + a_2 \frac{d^2y}{dx^2} + a_3 \frac{d^3y}{dx^3} + \cdots = 0. \qquad (12.10)$$

12.2.1 The Harmonic Oscillator

Consider an object that is suspended at the end of a coil spring whose other end is stationary. The object can oscillate in the z direction. Let $z = 0$ when the spring has its equilibrium length. If we can ignore gravity, the only force on the object is due to the spring and is given to a good approximation by *Hooke's law*,[3]

$$F_z = -kz, \qquad (12.11)$$

where k is a constant called the *spring constant*. The negative sign indicates a negative force when z is positive and vice versa, so that the force pushes the mass toward its equilibrium position. A real object on a spring is difficult to analyze exactly, because the spring also moves as it stretches and compresses and because Hooke's law is an approximation that fails when the spring is stretched beyond its elastic limit and when it is compressed enough that the coils interfere with each other. We now define the harmonic oscillator, which is a *model system* that approximately represents the object on the spring. A model system is a hypothetical system (existing only in our minds) that has some properties in common with a real system, but is enough simpler to allow mathematical analysis. The harmonic oscillator is defined by assuming that the spring has no mass and that Hooke's law is exactly obeyed, even if z has a large magnitude.

The Equation of Motion of the Harmonic Oscillator

Newton's second law gives the *equation of motion* for the harmonic oscillator:

$$m \frac{d^2z}{dt^2} = -kz. \qquad (12.12)$$

We divide by m and move all terms to the left-hand side of the equation to obtain

$$\frac{d^2z}{dt^2} + \frac{k}{m} z = 0. \qquad (12.13)$$

This is a homogeneous ordinary linear differential equation with constant coefficients. We say that it is *second order*, which means that the highest order derivative in the equation is a second derivative.

There are two important facts about linear homogeneous differential equations:

1. If $z(t)$ satisfies the equation, then $cz(t)$ is also a solution, where c is a constant.
2. If $z_1(t)$ and $z_2(t)$ are two functions that satisfy the equation, then the *linear combination* $z_3(t)$ is also a solution:

$$z_3(t) = c_1 z_1(t) + c_2 z_2(t), \qquad (12.14)$$

where c_1 and c_2 are constants.

Solution of the Equation of Motion

A homogeneous ordinary linear differential equation with constant coefficients can be solved as follows:

1. Assume the *trial solution*

$$z(t) = e^{\lambda t}, \qquad (12.15)$$

where λ is a constant.

[2] The acceleration due to gravity actually depends slightly on latitude, having a larger value near the poles. This value applies at the latitude of Washington, DC, and Seoul, South Korea.

[3] After Robert Hooke, 1635–1703, one of Newton's contemporaries and rivals.

2. Substitute the trail solution into the equation and produce an algebraic equation in λ called the *characteristic equation*.
3. Find the values of λ that satisfy the characteristic equation. For an equation of order n, there will be n values of λ, where n is the order of the equation. Call these values $\lambda_1, \lambda_2, \ldots, \lambda_n$. These values produce n versions of the trial solution that satisfy the equation.
4. Write the solution as a linear combination

$$z(t) = c_1\, e^{\lambda_1 t} + c_2\, e^{\lambda_2 t} + \cdots + c_n\, e^{\lambda_n t}. \qquad (12.16)$$

Example 12.2. Find a solution to the differential equation

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} + \frac{\mathrm{d}y}{\mathrm{d}x} - 2y = 0.$$

Substitution of the trial solution $y = e^{\lambda x}$ gives the equation

$$\lambda^2 e^{\lambda x} + \lambda\, e^{\lambda x} - 2\, e^{\lambda x} = 0.$$

Division by $e^{\lambda x}$ gives the characteristic equation.

$$\lambda^2 + \lambda - 2 = 0.$$

The solutions to this equation are

$$\lambda = 1, \quad \lambda = -2.$$

The solution to the differential equation is

$$y(x) = c_1\, e^{x} + c_2\, e^{-2x},$$

where c_{10} and c_2 are constants.

The solution in the previous example is a *family of solutions*, one solution for each set of values for c_1 and c_2. A solution to a linear differential equation of order n that contains n arbitrary constants is known to be a *general solution*, which is a family of functions that includes almost every solution to the differential equation. Our solution is a general solution, since it contains two arbitrary constants. A solution to a differential equation that contains no arbitrary constants is called a *particular solution*.

Exercise 12.2. Find the general solution to the differential equation

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} - 3\frac{\mathrm{d}y}{\mathrm{d}x} + 2y = 0.$$

We frequently have additional information that will enable us to pick a particular solution out of a family of solutions. Such information consists of knowledge of boundary conditions and initial conditions. *Boundary conditions* arise from physical requirements on the solution, such as conditions that apply to the boundaries of the region in space where the solution applies. *Initial conditions* arise from knowledge of the state of the system at some initial time.

We now apply the method to the solution of the equation of motion of the harmonic oscillator. We substitute the trial solution into Eq. (12.12):

$$\frac{\mathrm{d}^2 e^{\lambda t}}{\mathrm{d}t^2} + \frac{k}{m} e^{\lambda t} = 0, \qquad (12.17)$$

$$\lambda^2 e^{\lambda t} + \frac{k}{m} e^{\lambda t} = 0. \qquad (12.18)$$

Division by $e^{\lambda t}$ gives the characteristic equation

$$\lambda^2 + \frac{k}{m} = 0. \qquad (12.19)$$

The solution of the characteristic equation is

$$\lambda = \pm i \left(\frac{k}{m}\right)^{1/2}, \qquad (12.20)$$

where $i = \sqrt{-1}$, the imaginary unit.

The general solution is

$$z = z(t) = c_1 \exp\left[+i\left(\frac{k}{m}\right)^{1/2} t\right] + c_2 \exp\left[-i\left(\frac{k}{m}\right)^{1/2} t\right], \qquad (12.21)$$

where c_1 and c_2 are arbitrary constants. The solution must be real, because imaginary and complex numbers cannot represent physically measurable quantities. From a trigonometric identity

$$e^{i\omega t} = \cos(\omega t) + i\, \sin(\omega t), \qquad (12.22)$$

we can write

$$z = c_1 \left[\cos(\omega t) + i\, \sin(\omega t)\right] + c_2 \left[\cos(\omega t) - i\, \sin(\omega t)\right], \qquad (12.23)$$

where

$$\omega = \left(\frac{k}{m}\right)^{1/2}. \qquad (12.24)$$

We let $c_1 + c_2 = b_1$ and $i(c_1 - c_2) = b_2$.

$$z = b_1 \cos(\omega t) + b_2 \sin(\omega t). \qquad (12.25)$$

Exercise 12.3. Show that the function of Eq. (12.25) satisfies Eq. (12.12).

To obtain a particular solution, we require some *Initial conditions*. We require one initial condition to evaluate each arbitrary constant. Assume that we have the conditions at $t = 0$:

$$z(0) = 0, \tag{12.26a}$$

$$v_z(0) = v_0, \tag{12.27}$$

where v_0 is a constant. For our first initial conditions,

$$z(0) = 0 = b_1 \cos(0) + b_2 \sin(0) = b_1 = 0, \tag{12.28}$$

$$z(t) = b_2 \sin(\omega t). \tag{12.29}$$

The velocity is given by

$$v_z(t) = \frac{\mathrm{d}z}{\mathrm{d}t} = b_2 \omega \cos(\omega t). \tag{12.30}$$

From our second initial condition

$$v_z(0) = v(0) = b_2 \omega \cos(0) = b_2 \omega.$$

This gives

$$b_2 = \frac{v_0}{\omega}. \tag{12.31}$$

Our particular solution is

$$z(t) = \left(\frac{v_0}{\omega}\right) \sin(\omega t) \tag{12.32}$$

as depicted in Figure 12.1.

The motion given by this solution is called *uniform harmonic motion*. It is *periodic*, repeating itself over and over. During one period, the argument of the sine changes by 2π. We denote the *period* (the length of time required for one cycle of the motion) by τ:

$$2\pi = \omega\tau = \left(\frac{k}{m}\right)^{1/2} \tau, \tag{12.33}$$

$$\tau = 2\pi \left(\frac{m}{k}\right)^{1/2}. \tag{12.34}$$

The reciprocal of the period is called the *frequency*, denoted by ν[4]:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} = \frac{\omega}{2\pi}. \tag{12.35}$$

The frequency gives the number of oscillations per second. The *circular frequency* ω gives the rate of change of the argument of the sine or cosine function in radians per second.

Example 12.3. A mass of 0.100 kg is suspended from a spring with a spring constant $k = 1.50\ \mathrm{N\ m^{-1}}$. Find the frequency and period of oscillation.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} = \frac{1}{2\pi}\sqrt{\frac{1.50\ \mathrm{N\ m^{-1}}}{0.100\ \mathrm{kg}}} = 0.616\ \mathrm{s^{-1}},$$

$$\tau = \frac{1}{\nu} = 1.62\ \mathrm{s}.$$

The solution of the equation of motion of the harmonic oscillator illustrates a general property of classical equations of motion. If the equation of motion and the initial conditions are known, the motion of the system is determined as a function of time. We say that classical equations of motion are *deterministic*.

The Vibration of a Diatomic Molecule

The vibration of a diatomic molecule can be modeled as a harmonic oscillator. Since both nuclei move, the mass must be replaced by the *reduced mass*,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}, \tag{12.36}$$

where m_1 is the mass of one atom and m_2 is the mass of the other atom. The frequency of vibration is

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}. \tag{12.37}$$

Example 12.4. Calculate the frequency of vibration of a hydrogen fluoride molecule. The force constant k is equal to $966\ \mathrm{N\ m^{-1}} = 966\ \mathrm{J\ m^{-2}}$.

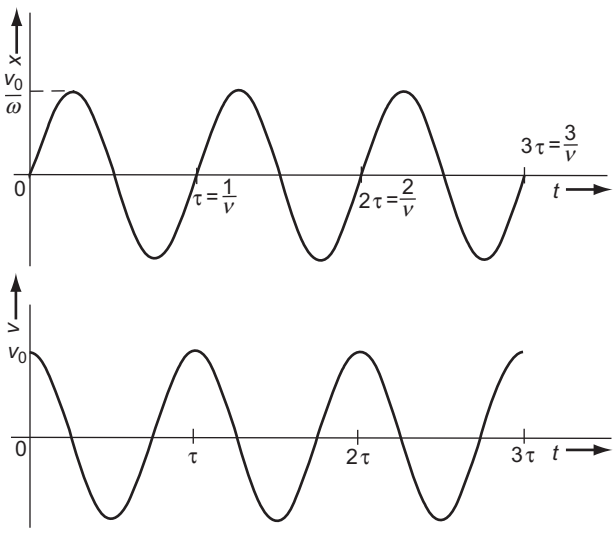


FIGURE 12.1 The position and velocity of a harmonic oscillator as functions of time.

[4] In some fonts, the Greek letter ν (nu) and the italic letter v (vee) look almost identical. Try not to be confused.

We can use average molar masses, since fluorine occurs with only one isotope and ordinary hydrogen is nearly all one isotope. We first calculate the reduced mass times Avogadro's constant :

$$\begin{aligned}\mu N_{\text{Av}} &= \frac{\left(1.008\text{ g mol}^{-1}\right)\left(18.998\text{ g mol}^{-1}\right)}{1.008\text{ g mol}^{-1}+18.998\text{ g mol}^{-1}}\left(\frac{1\text{ kg}}{1000\text{ g}}\right)\\ &= 9.572\times10^{-4}\text{ kg mol}^{-1}\\ \mu &= \frac{9.572\times10^{-4}\text{ kg mol}^{-1}}{6.02214\times10^{23}\text{ mol}^{-1}} = 1.589\times10^{-27}\text{ kg}\\ \nu &= \frac{1}{2\pi}\sqrt{\frac{966\text{ J m}^{-2}}{1.589\times10^{-27}\text{ kg}}}\\ &= \frac{1}{2\pi}\sqrt{\frac{966\text{ kg m}^2\text{ s}^{-2}\text{ m}^{-2}}{1.589\times10^{-27}\text{ kg}}} = 1.24\times10^{14}\text{ s}^{-1}\end{aligned}$$

Exercise 12.4. The frequency of vibration of the H_2 molecule is $1.3194\times10^{14}\text{ s}^{-1}$. Find the value of the force constant.

The Energy of a Harmonic Oscillator

The *kinetic energy* of the harmonic oscillator is

$$\mathcal{K} = \frac{1}{2}mv_z^2. \tag{12.38}$$

According to classical mechanics, if the force on an object depends only on its position, the force can be derived from a potential energy function. For an object moving only in the z direction

$$F_z = -\frac{\partial\mathcal{V}}{\partial z}, \tag{12.39}$$

where $\mathcal{V}$ is the potential energy. From the equation for the force, the *potential energy* of the harmonic oscillator must be given by

$$\mathcal{V}(z) = \frac{1}{2}kz^2. \tag{12.40}$$

The total energy is the sum of the kinetic energy and the potential energy

$$\begin{aligned}E &= \mathcal{K}+\mathcal{V}\\ &= \frac{1}{2}mv_0^2\cos^2(\omega t)+\frac{1}{2}k\left(\frac{v_0}{\omega}\right)^2\sin^2(\omega t) = \frac{1}{2}mv_0^2,\end{aligned} \tag{12.41}$$

where we have used the identity of Eq. (7) of Appendix B. As a harmonic oscillator moves, the kinetic energy rises and falls, but the potential energy changes so that the total energy remains constant. If the energy of a system remains constant during its motion, we say that the energy is *conserved*, and that the system is *conservative*. There is an important theorem of classical mechanics: *If the forces on the particles of a system can be obtained from a potential energy function, the system will be conservative.*

Example 12.5. A mass of 0.100 kg is suspended from a spring with a spring constant $k = 1.50\text{ N m}^{-1}$. If its amplitude of oscillation (the maximum value of z) is 0.120 m, find the energy of the oscillator. Find the maximum velocity.

At the maximum value of z , the energy is all potential energy:

$$\begin{aligned}E &= \mathcal{V}_{\max} = \frac{1}{2}kx_{\max}^2 = \frac{1}{2}\left(1.50\text{ N m}^{-1}\right)\left(0.120\text{ m}\right)^2\\ &= 0.0108\text{ N m} = 0.0108\text{ J}.\end{aligned}$$

When $z = 0$, the energy is all kinetic energy and the velocity has its maximum value:

$$\begin{aligned}E &= \mathcal{K}_{\max} = \frac{1}{2}mv_{\max}^2,\\ v_{\max} &= \sqrt{\frac{2E}{m}} = \sqrt{\frac{2\left(0.0108\text{ J}\right)}{0.100\text{ kg}}} = 0.465\text{ m s}^{-1}.\end{aligned}$$

Exercise 12.5. According to quantum mechanics, the energy of a harmonic oscillator is quantized. That is, it can take on any one of a certain set of values, given by

$$E = h\nu\left(\text{v}+\frac{1}{2}\right),$$

where h is Planck's constant, equal to 6.62608×10^{-34} J s, ν is the frequency and v is a quantum number, which can equal $0, 1, 2, \ldots$ The frequency of oscillation of a hydrogen molecule is $1.319\times10^{14}\text{ s}^{-1}$. If a classical harmonic oscillator having this frequency happens to have an energy equal to the v=1 quantum energy, find this energy. What is the maximum value that its kinetic energy can have in this state? What is the maximum value that its potential energy can have? What is the value of the kinetic energy when the potential energy has its maximum value?

12.2.2 The Damped Harmonic Oscillator—A Nonconservative System

The *damped harmonic oscillator* is a harmonic oscillator that is subject to an additional friction force that is proportional to the velocity and in the opposite direction:

$$\mathbf{F_f} = -\zeta\mathbf{v} = -\zeta\frac{\text{d}\mathbf{r}}{\text{d}t}, \tag{12.42}$$

where ζ is called the *friction constant*. An example of such a force is the frictional force on a spherical object moving relatively slowly through a viscous fluid. Since this force

cannot be derived from a potential energy, the system is not conservative and its energy will change with time.

If the oscillator moves only in the z direction, the equation of motion is

$$-\zeta\frac{dz}{dt}-kz=m\left(\frac{d^2z}{dt^2}\right). \tag{12.43}$$

This equation is a linear homogeneous equation with constant coefficients, so a trial solution of the form of Eq. (12.15) will work. Substitution of the trial solution into the equation gives

$$-\zeta\lambda e^{\lambda t}-ke^{\lambda t}=m\lambda^2e^{\lambda t}.$$

Division by $me^{\lambda t}$ gives the characteristic equation

$$\lambda^2+\frac{\zeta\lambda}{m}+\frac{k}{m}=0. \tag{12.44}$$

From the quadratic formula, the two solutions of this equation are

$$\lambda_1=-\frac{\zeta}{2m}+\frac{\sqrt{(\zeta/m)^2-4k/m}}{2}, \tag{12.45}$$

$$\lambda_2=-\frac{\zeta}{2m}-\frac{\sqrt{(\zeta/m)^2-4k/m}}{2} \tag{12.46}$$

and the general solution to the differential equation is

$$z(t)=c_1\,e^{\lambda_1 t}+c_2\,e^{\lambda_2 t}. \tag{12.47}$$

Exercise 12.6. Show that $e^{\lambda_1 t}$ does satisfy the differential equation.

Greater than Critical Damping

There are three cases: In the first case, the quantity inside the square root in Eq. (12.45) is positive, so that λ_1 and λ_2 are both real. Since ζ, k, and m are all positive, this corresponds to a relatively large value of the friction constant ζ,

$$\begin{aligned}(\zeta/m)^2&\succ\frac{4k}{m},\\ \frac{\zeta}{m}&\succ\sqrt{\frac{4k}{m}},\\ \zeta&\succ\sqrt{4km}.\end{aligned} \tag{12.48}$$

This case is called *greater than critical damping*. In this case, the mass at the end of the spring does not oscillate, but returns smoothly to its equilibrium position of $z=0$ if disturbed from this position. The values of the constants c_1 and c_2 must be determined for a particular case.

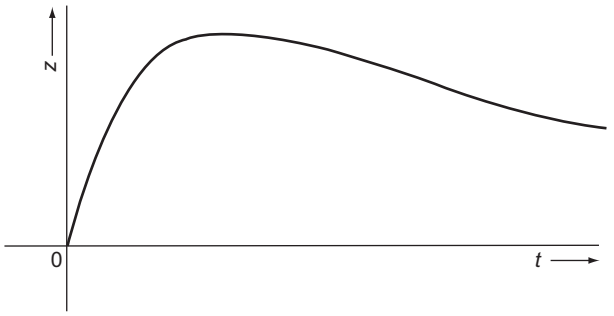


FIGURE 12.2 The position of a greater than critically damped harmonic oscillator as a function of time.

Figure 12.2 shows the position of a greater than critically damped oscillator as a function of time for the case that $c_1=-c_2$ so that $z=0$ at $t=0$. Since the two terms decay at different rates, the oscillator moves away from $z=0$ and then returns smoothly toward $z=0$.

Example 12.6. From the fact that ζ, k, and m are all positive, show that λ_1 and λ_2 are both negative in the case of greater than critical damping, and from this fact, show that

$$\lim_{t\to\infty}z(t)=0,$$

$$\lambda_2=-\frac{\zeta}{2m}-\frac{\sqrt{(\zeta/m)^2-4k/m}}{2}.$$

Since $(\zeta/m)^2$ is larger than $4k/m$

$$(\zeta/m)^2-4k/m\succ 0$$

the square root in the second term is real and the second term is negative. Therefore λ_2 must be negative,

$$\lambda_1=-\frac{\zeta}{2m}+\frac{\sqrt{(\zeta/m)^2-4k/m}}{2}.$$

Since the second term is positive, we need to show that it is smaller in magnitude than the first term. Square each term. We must have

$$\frac{\zeta^2}{4m^2}\succ\frac{(\zeta/m)^2-4k/m}{4}.$$

Subtract $\zeta^2/2m^2$ from each side of this inequality. This does not change the sense of the inequality

$$0\succ-\frac{k}{m}.$$

This is obviously correct, so λ_1 must also be negative. Both terms in (12.47) approach zero for large values of the time.

Less than Critical Damping

The next case is that of small values of the friction constant ζ, which is called *less than critical damping*. If

$$\left(\frac{\zeta}{m}\right)^2 < \frac{4k}{m},$$

the quantity inside the square root in Eq. (12.45) is negative, so that λ_1 and λ_2 are complex quantities:

$$\lambda_1 = -\frac{\zeta}{2m} + i\omega, \tag{12.49}$$

$$\lambda_2 = -\frac{\zeta}{2m} - i\omega, \tag{12.50}$$

where we let

$$\omega = \sqrt{\frac{k}{m} - \left(\frac{\zeta}{2m}\right)^2}. \tag{12.51}$$

The solution thus becomes

$$z(t) = c_1\, e^{i\omega t} e^{-\zeta t/2m} + c_2\, e^{-i\omega t} e^{-\zeta t/2m}. \tag{12.52}$$

Using Eq. (21) in Appendix B, we can write

$$z(t) = \left[b_1 \cos(\omega t) + b_2 \sin(\omega t)\right] e^{-\zeta t/2m}. \tag{12.53}$$

This shows *z(t)* to be an oscillatory function times an exponentially decreasing function, giving the "ringing" behavior shown in Figure 12.3.

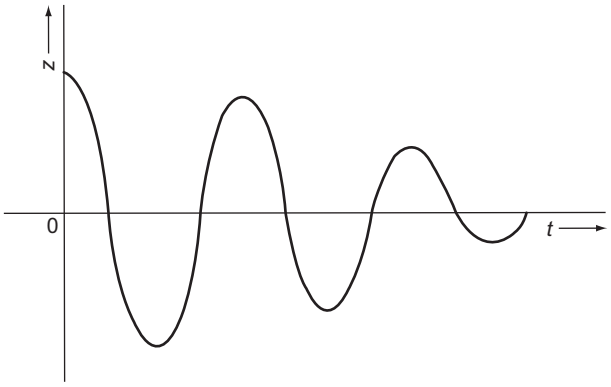


FIGURE 12.3 The position of a less than critically damped oscillator as a function of time for the case that $b_2 = 0$ and the initial conditions are that $z(0) = z_0$ and that $v_z(0) = 0$.

Exercise 12.7. If $z(0) = z_0$ and if $v_z(0) = 0$, express the constants b_1 and b_2 in terms of z_0.

Critical Damping

The final case is that of *critical damping*. In this case the quantity inside the square root in Eq. (12.45) is equal to zero. This is not likely to happen by chance, but it is possible to construct an oscillating object such as a galvanometer mirror or a two-pan balance beam that is very nearly critically damped by a magnetic field. The condition for critical damping is

$$\left(\frac{\zeta}{2m}\right)^2 = \frac{k}{m}. \tag{12.54}$$

In the case of critical damping the two values of λ are equal to each other,

$$\lambda_1 = \lambda_2 = -\frac{\zeta}{2m}, \tag{12.55}$$

so that

$$z(t) = \left(c_1 + c_2\right) e^{\lambda t} = c e^{\lambda t}, \tag{12.56}$$

where c is the sum of the two constants c_1 and c_2 and where we drop the subscript on λ. A general solution for a second-order linear equation contains two arbitrary constants, and a sum of two constants does not constitute two separate constants. Since we do not have a general solution, there must be another family of solutions. We attempt additional trial functions until we find one that works. The one that works is

$$z(t) = te^{\lambda t}. \tag{12.57}$$

Exercise 12.8. Substitute this trial solution into Eq. (12.43), using the condition of Eq. (12.54), and show that the equation is satisfied.

Our general solution is now

$$z(t) = \left(c_1 + c_2 t\right) e^{\lambda t}, \tag{12.58}$$

where we omit the subscript on λ. The velocity is given by

$$v_z(t) = \frac{\mathrm{d}z}{\mathrm{d}t} = c_1\, \lambda e^{\lambda t} + c_2\, e^{\lambda t} + c_2\, t\lambda e^{\lambda t}.$$

For any set of initial conditions, we can find the appropriate values of c_1 and c_2. The behavior of a critically damped oscillator is much the same as that of Figure 12.2, with no oscillation.

Example 12.7. Consider a critically damped oscillator with $\lambda = -1.00\ \mathrm{s}^{-1}$. Assume that its initial position is $z(0) = 0.00$ m and that its initial velocity is $1.00\ \mathrm{m\ s}^{-1}$. Find its position and velocity at $t = 2.00$ s.

In order for $z\left(0\right)$ to equal 0.00 m , we must require that $c_1 = 0.0$ m. The velocity is then given by

$$v_z(t) = c_2\, e^{\lambda t} + c_2\, t\lambda e^{\lambda t}.$$

The velocity at $t = 0$ is

$$\begin{aligned} v_z(0) &= c_2 = 1.00\ \mathrm{m\ s}^{-1}, \\ z(t) &= \left(1.00\ \mathrm{m\ s}^{-1}\right)\left[\left(1.00\ \mathrm{s}^{-1}\right)t\right] \\ &\quad \times \exp\left[-(1.00\ \mathrm{s}^{-1})t\right]. \end{aligned}$$

The position at $t = 2.00$ s is

$$z(2.00\text{ s}) = c_2\, t e^{\lambda t} = (1.00\text{ m s}^{-1})(2.00\text{ s})e^{-2.00} = 0.2707\text{ m},$$

the velocity at $t = 2.00$ s is

$$v_z(2.00\text{ s}) = \left(1.00\text{ m s}^{-1}\right) e^{-2.00} + (1.00\text{ m s}^{-1})\left(-1.00\text{ s}^{-1}\right)\left(2.00\text{ s}\right) e^{-2.00} = -0.2707\text{ m s}^{-1}.$$

Figure 12.4 shows the position of the critically damped oscillator in this example as a function of time.

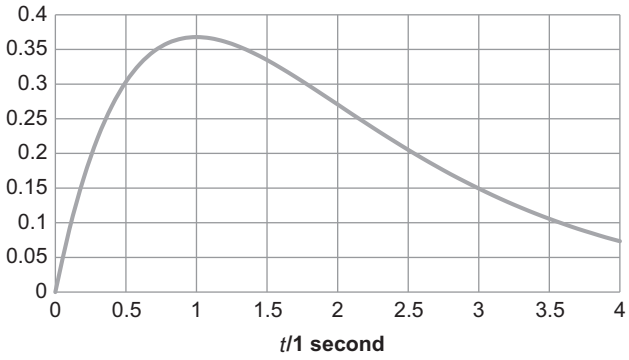


FIGURE 12.4 The position of the critically damped oscillator as a function of time.

Exercise 12.9. Locate the time at which z attains its maximum value and find the maximum value.

12.3 INHOMOGENEOUS LINEAR DIFFERENTIAL EQUATIONS: THE FORCED HARMONIC OSCILLATOR

An *inhomogeneous differential equation* contains a term that is not proportional to the unknown function or to any of its derivatives. An example of a linear inhomogeneous equation is

$$f_3(t)\frac{\mathrm{d}^3 z}{\mathrm{d}t^3} + f_2(t)\frac{\mathrm{d}^2 z}{\mathrm{d}t^2} + f_1(t)\frac{\mathrm{d}z}{\mathrm{d}t} = g(t), \qquad (12.59)$$

where $f_3 f_2, f_1$, and g are some functions of t but do not depend on z. The term *g(t)* is the *inhomogeneous term.* If an external force *F(t)* is exerted on a harmonic oscillator, the oscillator is called a *forced harmonic oscillator*. If the external force depends only on the time, the equation of motion is an inhomogeneous differential equation with constant coefficients:

$$m\frac{\mathrm{d}^2 z}{\mathrm{d}t^2} = -kz + F(t). \qquad (12.60)$$

We divide by m:

$$\frac{\mathrm{d}^2 z}{\mathrm{d}t^2} + \frac{k}{m}z = \frac{F\left(t\right)}{m}. \qquad (12.61)$$

The term $F(t)/m$ is the inhomogeneous term.

A method for solving such an inhomogeneous equation is:

Step 1. Solve the equation obtained by deleting the inhomogeneous term. This homogeneous equation is called the *complementary equation*, and the general solution to this equation is called the *complementary function,* z_c.

Step 2. Find a particular solution, z_p, to the inhomogeneous equation by whatever means may be necessary.

Step 3. The sum of the complementary function and this particular solution is the general solution to the inhomogeneous equation.

Exercise 12.10. If $z_c(t)$ is a general solution to the complementary equation and $z_p(t)$ is a particular solution to the inhomogeneous equation, show that $z_c + z_p$ is a solution to the inhomogeneous equation of Eq. (12.59).

12.3.1 Variation of Parameters Method

This is a method for finding a particular solution to a linear inhomogeneous equation. If the inhomogeneous term is a power of t, an exponential, a sine, a cosine, or a combination of these functions, this method can be used. One proceeds by taking a suitable trial function that contains parameters (constants whose values need to be determined). This trial function is substituted into the inhomogeneous equation and the values of the parameters are found so that the inhomogeneous equation is satisfied. Table 12.1 gives a list of suitable trial functions for various inhomogeneous terms.

The trial solution given in this table will not work if the characteristic equation for the complementary differential equation has a root equal to the forbidden characteristic root. If such a root occurs with multiplicity k , multiply the trial solution by t^k to obtain a trial solution that will work.

Example 12.8. Assume that the external force on a forced harmonic oscillator is given by

$$F(t) = F_0 \sin(\alpha t),$$

where F_0 and α are constants. Find the general solution to the equation of motion.

The equation of motion is

$$\frac{\mathrm{d}^2 z}{\mathrm{d}t^2} + \frac{k}{m}z = \frac{F_0 \sin(\alpha t)}{m}. \qquad (12.62)$$

The solution to the complementary equation is the same as for the unforced harmonic oscillator:

$$z_c = b_1 \cos(\omega t) + b_2 \sin(\omega t).$$

TABLE 12.1 Particular Trial Solutions for the Variation of Parameters

Inhomogeneous term	Trial solution	Forbidden characteristic root
1	A	0
t^n	$A_0 + A_1 t + A_2 t + \cdots + A_n t^n$	0
$e^{\alpha t}$	$Ae^{\alpha t}$	α
$t^n e^t$	$e^{\alpha t}(A_0 + A_1 t + A_2 t + \cdots + A_n t^n)$	α
$e^{\alpha t}\sin(\beta t)$	$e^{\alpha t}[A\cos(\beta t) + B\sin(\beta t)]$	α,β
$e^{\alpha t}\cos(\beta t)$	$e^{\alpha t}[A\cos(\beta t) + B\sin(\beta t)]$	α,β

Use of Table 12.1 gives the particular solution

$$z_{\mathrm{p}} = A\cos(\alpha t) + B\sin(\alpha t).$$

Substitution of this into the inhomogeneous equation gives

$$\begin{aligned}
&-\alpha^2 A\cos(\alpha t) - \alpha^2 B\sin(\alpha t)\\
&+\frac{k}{m}\left[A\cos(\alpha t) + B\sin(\alpha t)\right]\\
&\quad = \frac{F_0\sin(\alpha t)}{m},\\
&(\omega^2-\alpha^2)A\cos(\alpha t) + \left(\omega^2-\alpha^2\right)B\sin(\alpha t)\\
&\quad = \frac{F_0\sin(\alpha t)}{m},
\end{aligned}$$

where we have replaced k/m by ω^2. This can be a valid equation for all values of t only if $A = 0$ and if

$$B = \frac{F_0}{m(\omega^2-\alpha^2)}.$$

The particular solution is

$$z_{\mathrm{p}}(t) = \frac{F_0}{m(\omega^2-\alpha^2)}\sin\left(\alpha t\right).$$

The general solution is

$$z(t) = b_1\cos(\omega t) + b_2\sin(\omega t) + \frac{F_0}{m(\omega^2-\alpha^2)}\sin\left(\alpha t\right), \tag{12.63}$$

where the constants b_1 and b_2 are to be determined by the initial conditions. Let us assume that $z(0) = 0$, so that $b_1 = 0$.

$$\begin{aligned}
z(t) &= b_2\sin(\omega t) + \frac{F_0}{m(\omega^2-\alpha^2)}\sin\left(\alpha t\right),\\
v_z(t) &= \frac{\mathrm{d}z}{\mathrm{d}t} = b_2\omega\cos(\omega t) + \frac{F_0\alpha}{m(\omega^2-\alpha^2)}\cos\left(\alpha t\right).
\end{aligned}$$

The constant b_2 would be determined by another initial condition on $v_z(0)$

$$\begin{aligned}
v_z(0) &= b_2\omega + \frac{F_0\alpha}{m(\omega^2-\alpha^2)},\\
b_2 &= \frac{v_z(0)}{\omega} - \frac{F_0\alpha}{m\omega(\omega^2-\alpha^2)}.
\end{aligned}$$

Exercise 12.11. Find an expression for the initial velocity.

The solution in the previous example is a linear combination of the natural motion and a motion proportional to the external force. If the frequencies of these are not very different, a motion such as shown in Figure 12.5, known as *beating*, can result. There is a periodic variation of the amplitude of vibration with a circular frequency equal to $\omega - \alpha$. You can hear this beating when a piano is being tuned. There are two or three strings for each note, and they are tuned separately. Each string can excite a sympathetic vibration in the other, which acts as an external force. When the frequencies of two strings are slightly different, you can hear a pulsation like that in Figure 12.5, which shows the case that $\alpha = 1.100\omega$.

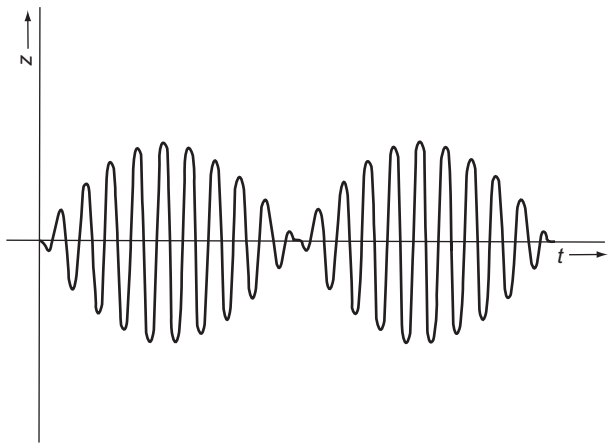


FIGURE 12.5 The position of a forced harmonic oscillator as a function of time for the case $\alpha = 1.1\omega$.

12.4 DIFFERENTIAL EQUATIONS WITH SEPARABLE VARIABLES

In this section we discuss equations that can be manipulated algebraically into the form

$$g(y)\frac{dy}{dx} = f(x), \tag{12.64}$$

where *g(y)* is a known integrable function of *y, f(x)* is a known integrable function of *x*, and *y(x)* is the unknown function. To solve Eq. (12.64), we symbolically multiply both sides of the equation by d*x* and use the relation:

$$\frac{dy}{dx}dx = dy. \tag{12.65}$$

We now have

$$g(y)dy = f(x)dx. \tag{12.66}$$

If we have manipulated the equation into this form, we say that we have *separated the variables*, because we have no *x* dependence in the left-hand side of the equation and no *y* dependence in the right-hand side. We can perform an indefinite integration on both sides of this equation to obtain

$$\int g(y)dy = \int f(x)dx + C, \tag{12.67}$$

where *C* is the difference of two constants of integration. We could do a definite integration

$$\int_{y_1}^{y_2} g(y)dy = \int_{x_1}^{x_2} f(x)dx, \tag{12.68}$$

where

$$y_1 = y(x_1), \tag{12.69}$$

$$y_2 = y(x_2). \tag{12.70}$$

The result of this integration is an algebraic equation that can be solved for *y* as a function of *x*.

Example 12.9. In a *first-order chemical reaction* with no back reaction, the concentration of the reactant is governed by

$$-\frac{dc}{dt} = kc,$$

where *c* is the concentration of the single reactant, *t* is the time, and *k* is a function of temperature called the *rate constant*. Solve the equation to find *c* as a function of *t*.

We divide by *c* and multiply by d*t* to separate the variables:

$$\frac{1}{c}\frac{dc}{dt}dt = \frac{1}{c}dc = -k\,dt.$$

We perform an indefinite integration

$$\int \frac{1}{c}dc = \ln(c) = -k\int dt + C = -kt + C,$$
$$\ln(c) = -kt + C,$$

where *C* is a constant of integration. We take the exponential of each side of this equation to obtain

$$e^{\ln(c)} = c = e^C e^{-kt} = c(0)e^{-kt},$$
$$c(t) = c(0)e^{-kt}. \tag{12.71}$$

A definite integration can be carried out instead of an indefinite integration:

$$\int_{c(0)}^{c(t_1)} \frac{1}{c}dc = \ln\left(\frac{c(t_1)}{c(0)}\right) = -k\int_0^{t_1} dt = -kt_1.$$

The limits on the two definite integrations must be done correctly. If the lower limit of the time integration is zero, the lower limit of the concentration integration must be the value of the concentration at zero time. The upper limit is similar.

Exercise 12.12. In a *second-order chemical reaction* involving one reactant and having no back reaction,

$$-\frac{dc}{dt} = kc^2.$$

Solve this differential equation by separation of variables. Do a definite integration from $t = 0$ to $t = t_1$.

If you are faced with a differential equation and if you think that there is some chance that separation of variables will work, try the method. If it doesn't work, you haven't lost very much time.

12.5 EXACT DIFFERENTIAL EQUATIONS

Sometimes an equation can be manipulated into the *Pfaffian form*:

$$M(x,y)dx + N(x,y,)dy = 0. \tag{12.72}$$

Some such differential forms are *exact*, which means that they are differentials of functions, as explained in Chapter 8. Other differentials are *inexact* , which means that they are not differentials of any function. If the differential is exact, the equation is called an *exact differential equation*. The test for exactness is based on the *Euler reciprocity relation*, as in Eq. (8.29): If

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y, \tag{12.73}$$

then the differential is exact. If the differential equation is exact, there is a function *f(x,y)* such that

$$\mathrm{d}f = M(x,y)\mathrm{d}x + N(x,y)\mathrm{d}y = 0, \tag{12.74}$$

which implies that

$$f(x,y) = k, \tag{12.75}$$

where k is a constant, because a constant function has a differential that vanishes. This equation can be solved for y in terms of x, providing a solution to the differential equation.

In Chapter 9 we discussed the procedure for finding the function in Eq. (12.75) by using a line integral,

$$f(x_1,y_1) = f(x_0,y_0) + \int_C \mathrm{d}f, \tag{12.76}$$

where C represents a curve beginning at (x_0,y_0) and ending at (x_1,y_1). A convenient curve is the rectangular path from (x_0,y_0) to (x_1,y_0) and then to (x_1,y_1). On the first part of this path, y is constant at y_0, so the dy integral vanishes and y is replaced by y_0 in the dx integral. On the second part of the path, x is constant at x_1, so the dx integral vanishes and x is replaced by x_1 in the dy integral:

$$\begin{aligned} f(x_1,y_1) = f(x_0,y_0) &+ \int_{x_0}^{x_1} M(x,y_0)\mathrm{d}x \\ &+ \int_{y_0}^{y_1} N(x_1,y)\mathrm{d}y. \end{aligned} \tag{12.77}$$

Both integrals are now ordinary integrals. If we can perform the integrations, we will have an algebraic equation that can be solved for y as a function of x. The solution will contain an arbitrary constant, because the same constant can be added to $f(x_1,y_1)$ and $f(x_0,y_0)$ in Eq. (12.77) without changing the equality.

Example 12.10. Solve the differential equation

$$2xy\,\mathrm{d}x + x^2\,\mathrm{d}y = 0.$$

The equation is exact, because

$$\frac{\partial}{\partial y}(2xy) = 2x \quad \text{and} \quad \frac{\partial}{\partial x}(x^2) = 2x,$$

so that the Pfaffian form is the differential of a function $f=f(x,y)$.We do a line integral from (x_0,y_0) to (x_1,y_0) and then to (x_0,y_1):

$$\begin{aligned} f(x_1,y_1) - f(x_0,y_0) &= \int_{x_0}^{x_1} 2xy_0\,\mathrm{d}x + \int_{y_0}^{y_1} x_1^2\,\mathrm{d}y = 0 \\ &= y_0x_1^2 - y_0x_0^2 + x_1^2y_1 - x_1^2y_0 = 0 \\ &= x_1^2y_1 - x_0^2y_0 = 0, \end{aligned}$$

where k is a constant. We drop the subscripts on x_1 and y_1 and consider x_0 and y_0 to be constants:

$$f(x,y) = x^2y = k,$$

where k is a constant. We solve this algebraic equation to obtain our general solution:

$$y = k/x^2.$$

Some condition would have to be specified to obtain the value of k.

Exercise 12.13. Solve the equation $(4x+y)\mathrm{d}x+x\,\mathrm{d}y = 0$.

12.6 SOLUTION OF INEXACT DIFFERENTIAL EQUATIONS USING INTEGRATING FACTORS

If we have an *inexact differential equation*

$$M(x,y)\mathrm{d}x + N(x,y)\mathrm{d}y = 0, \tag{12.78}$$

we cannot use the method of the previous section. However, some inexact differentials yield an exact differential when multiplied by a function known as an *integrating factor*. If the function $g(x,y)$ is an integrating factor for the differential in Eq. (12.78), then

$$g(x,y)M(x,y)\mathrm{d}x + g(x,y)N(x,y)\mathrm{d}y = 0 \tag{12.79}$$

is an exact differential equation that can be solved by the method of the previous section. A solution for Eq. (12.79) will also be a solution for Eq. (12.78).

Example 12.11. Solve the differential equation

$$\frac{\mathrm{d}y}{\mathrm{d}x} = \frac{y}{x}.$$

We convert the equation to the Pfaffian form,

$$y\,\mathrm{d}x - x\,\mathrm{d}y = 0.$$

We test for exactness:

$$\begin{aligned} \left(\frac{\partial_y}{\partial_y}\right)_x &= 1, \\ \left[\frac{\partial(-x)}{\partial x}\right]_y &= -1. \end{aligned}$$

The equation is not exact. We now show that $1/x^2$ is an integrating factor. Multiplication by this factor gives

$$\left(\frac{y}{x^2}\right)\mathrm{d}x - \left(\frac{1}{x}\right)\mathrm{d}y = 0.$$

This is an exact differential of a function $f = f(x, y)$, since

$$\left[\frac{\partial(y/x^2)}{\partial y}\right]_x = \frac{1}{x^2},$$
$$\left[\frac{\partial(-1/x)}{\partial x}\right]_y = \frac{1}{x^2}.$$

We can solve this equation by the method of the previous section:

$$\begin{aligned} f(x_1, y_1) - f(x_0, y_0) &= s\int_{x_0}^{x_1} \frac{y_0}{x^2}\,dx - \int_{y_0}^{y_1} \frac{1}{x_1}\,dy = 0 \\ &= -\frac{y_0}{x_1} + \frac{y_0}{x_0} - \frac{y_1}{x_1} + \frac{y_0}{x_1} = 0 \\ &= \frac{y_0}{x_0} - \frac{y_1}{x_1} = 0. \end{aligned}$$

We regard x_0 and y_0 as constants, so that

$$\frac{y}{x} = \frac{y_0}{x_0} = k,$$

where k is a constant. We solve for y in terms of x to obtain the solution

$$y = kx.$$

This is a general solution, since the original equation was first order and the solution contains one arbitrary constant.

If an inexact differential has one integrating factor, it has been shown that it has an infinite number of integrating factors. Unfortunately, there is no general procedure for finding an integrating factor except by trial and error.

Exercise 12.14. Show that $1/y^2$ is an integrating factor for the equation in the previous example and show that it leads to the same solution.

12.7 PARTIAL DIFFERENTIAL EQUATIONS

Differential equations that contain partial derivatives are called *partial differential equations.* These equations involve functions of several independent variables.

12.7.1 Waves in a String

We consider the classical equation of motion of a *flexible string*. There are important similarities between this equation and the Schrödinger equation of quantum mechanics. The flexible string is a model system designed to provide an approximate representation of a real string such as those found in musical instruments. This flexible string is defined as follows:

1. It is completely flexible, so that no force is required to bend the string.
2. Its motion is restricted to small vibrations, so that the string is not appreciably stretched.
3. It has a finite length and both ends of the string are fixed in position.

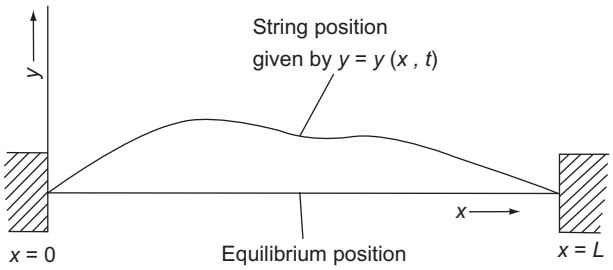


FIGURE 12.6 A flexible string.

Figure 12.6 depicts the string. We use the equilibrium (straight) position of the string as our x axis and let one end of the string be at $x = 0$ and the other end of the string be at $x = L$. The displacement of the string from its equilibrium position in the y direction is denoted by $y(x, t)$ and the displacement in the z direction is denoted by $z(x,t)$.

The equation of motion of the string is derived by writing Newton's second law for a small segment of the string and taking a mathematical limit as the length of the segment becomes infinitesimal.[5] The motions in the y and z directions are independent of each other and can be solved separately. The equation of motion for the y direction is

$$\left(\frac{\partial^2 y}{\partial t^2}\right) = \frac{T}{\rho}\left(\frac{\partial^2 y}{\partial x^2}\right) = c^2\left(\frac{\partial^2 y}{\partial x^2}\right), \tag{12.80}$$

where T is the magnitude of the tension force on the string and ρ is the mass of the string per unit length. We let

$$c = \sqrt{\frac{T}{\rho}}. \tag{12.81}$$

12.7.2 Solution by Separation of Variables

We seek a solution that can be written as a product of factors, each of which depends on only one variable:

$$y(x,t) = \psi(x)\theta(t). \tag{12.82}$$

This is called a *solution with the variables separated*. We regard it as a *trial solution* and substitute it into the differential equation. This method of separation of variables is slightly different from our previous version, since we are

[5] Robert G. Mortimer, *Physical Chemistry*, 3rd ed., Elsevier, 2008, pp. 1268–1269.

now separating two independent variables instead of one independent variable and one dependent variable.

Since ψ does not depend on t and θ does not depend on x, the result of substituting the trial solution into Eq. (12.80) is

$$\psi(x)\left(\frac{\mathrm{d}^2\theta}{\mathrm{d}t^2}\right) = c^2\theta(t)\left(\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\right). \tag{12.83}$$

We write ordinary derivatives since we now have functions of only one variable. We separate the variables by dividing both sides of Eq. (12.83) by the product $\psi(x)\theta(t)$. We also divide by c^2:

$$\frac{1}{c^2\theta(t)}\frac{\mathrm{d}^2\theta}{\mathrm{d}t^2} = \frac{1}{\psi(x)}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}. \tag{12.84}$$

We now use the fact that x and t are mathematically independent variables. If we temporarily keep t fixed at some value, the left-hand side of Eq. (12.84) is equal to a constant. We can still allow x to vary, so the right-hand side of the equation must be a constant function of x. We equate it to the constant $-\kappa^2$:

$$\frac{1}{\psi(x)}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\kappa^2 = \text{constant}. \tag{12.85}$$

For the same reason, the left-hand side must be a constant function of t, and must equal the same constant:

$$\frac{1}{c^2\theta(t)}\frac{\mathrm{d}^2\theta}{\mathrm{d}t^2} = -\kappa^2. \tag{12.86}$$

We denote the constant by the symbol $-\kappa^2$ because this choice will make κ into a real quantity. We now multiply Eq. (12.85) by $\psi(x)$ and multiply Eq. (12.86) by $c^2\theta(t)$. We obtain

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \kappa^2\psi = 0 \tag{12.87}$$

and

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}t^2} + \kappa^2c^2\theta = 0. \tag{12.88}$$

The separation of variables is complete, and we have two ordinary differential equations. Except for the symbols used, both of these equations are the same as Eq. (12.12). We transcribe the real solution to that equation with appropriate changes in symbols:

$$\psi(x) = a_1\cos(\kappa x) + a_2\sin(\kappa x), \tag{12.89}$$

$$\theta(t) = b_1\cos(\kappa ct) + b_2\sin(\kappa ct). \tag{12.90}$$

These are general solutions to the ordinary differential equations of Eqs. (12.87) and (12.88), but we do not necessarily have a general solution to our partial differential equation, because there can be solutions that are not of the form of Eq. (12.82).

We can evaluate the constants to make the solution apply to a specific case. We have the *boundary conditions* that $y(0) = 0$ and $y(L) = 0$. If y must vanish at $x = 0$ and at $x = L$, then ψ must vanish at these points, since the factor θ does not depend on x:

$$\psi(0) = 0 \tag{12.91}$$

and

$$\psi(L) = 0. \tag{12.92}$$

Equation (12.91) requires that

$$a_1 = 0, \tag{12.93}$$

since $\cos(0) = 1$ and $\sin(0) = 0$. Since $\sin(0) = 0$, the condition of Eq. (12.91) is satisfied. Equation (12.92) requires that

$$\sin(\kappa L) = 0. \tag{12.94}$$

We know that

$$\sin(n\pi) = 0 \quad (n = 0,1,2,\ldots), \tag{12.95}$$

where n is some integer. Therefore,

$$\kappa = \frac{n\pi}{L} \quad (n = 1,2,3,\ldots). \tag{12.96}$$

We are not interested in the case that $n = 0$, because this corresponds to a stationary string at its equilibrium position. Negative values of n simply change the sign of the function, which is irrelevant.

The coordinate factor ψ in our solution is now

$$\psi(x) = a_2\sin\left(\frac{n\pi x}{L}\right). \tag{12.97}$$

To determine the time-dependent factor θ, we apply *initial conditions.* Let us assume that at $t = 0$, the string is passing through its equilibrium position, which corresponds to $y = 0$ for all x. If so, then $b_1 = 0$ since $\cos(0) = 1$. We now have

$$\theta = b_2\sin\left(\frac{n\pi ct}{L}\right).$$

The complete solution is

$$y(x,t) = A\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi ct}{L}\right), \tag{12.98}$$

where we write $A = a_2b_2$. The maximum *amplitude* (maximum value of y) is equal to A, and another initial condition would be required to specify its value.

We have a set of solutions, one for each value of the integer n. Figure 12.7 shows the function $\psi(x)$ for several values of n. Each curve represents the shape of the string at an instant when $\theta(t) = 1$. At other times, the string is vibrating between such a position and a position given

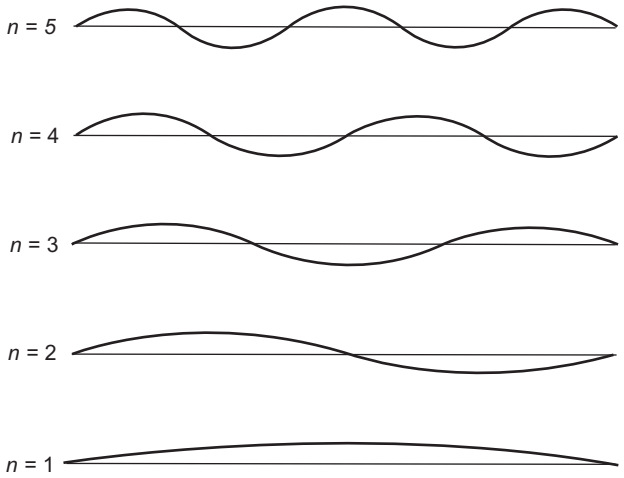


FIGURE 12.7 Standing waves in a flexible string.

by $-\psi(x)$. There are fixed points at which the string is stationary. These points are called *nodes*, and the number of nodes other than the two nodes at the ends of the string is equal to $n-1$. A wave with stationary nodes is called a *standing wave*.

We let λ represent the *wavelength*, or the distance for the sine function in ψ to go through a complete period:

$$n\lambda = 2L. \tag{12.99}$$

The *period* of oscillation is the time required for the sine function in the factor $\theta(t)$ to go through a complete oscillation and return the string to its original position and velocity, which requires the argument of the sine function to range through 2π. If τ represents the period,

$$\frac{n\pi c\tau}{L} = 2\pi; \quad \tau = \frac{2L}{nc}. \tag{12.100}$$

The *frequency* ν is the reciprocal of the period:

$$\nu = \frac{nc}{2L} = \left(\frac{n}{2L}\right)\left(\frac{T}{\rho}\right)^{1/2}. \tag{12.101}$$

In musical acoustics, the oscillation corresponding to $n=1$ is called the *fundamental*, that for $n=2$ is the *first overtone*, and so on. The fundamental is also called the *first harmonic*, the first overtone is called the *second harmonic*, and so on.

Exercise 12.15. A certain violin string has a mass per unit length of 20.00 mg cm^{-1} and a length of 55.0 cm. Find the tension force necessary to make it produce a fundamental tone of A above middle C (440 oscillations per second = 440 s^{-1} = 440 Hz).

When a string in a musical instrument is struck or bowed, it will usually not vibrate according to a single harmonic. The following Fourier series is a linear combination that satisfies Eq. (12.80) and can represent any possible motion of the string:

$$y(x,t) = \sum_{n=1}^{\infty} \sin\left(\frac{n\pi x}{L}\right)\left[a_n \cos\left(\frac{n\pi ct}{L}\right) + b_n \sin\left(\frac{n\pi ct}{L}\right)\right]. \tag{12.102}$$

This is a Fourier series in time with coefficients that depend on position. The fact that a linear combination of solutions can be a solution to the equation is an example of the *principle of superposition*. We can regard the linear combination as a physical representation of *constructive* and *destructive interference* of the different harmonics. The strengths of the different harmonics are represented by the values of the coefficients a_n and b_n. Different musical instruments have different relative strengths of different harmonics.

For a string of finite length with fixed ends, only standing waves can occur. For an infinitely long string, traveling waves can also occur. In a traveling wave, nodes move along the string. A traveling wave does not generally correspond to a solution with the variables separated. The following wave function represents a *traveling wave*:

$$y(x,t) = A\sin\left[k(x-ct)\right]. \tag{12.103}$$

Example 12.12. Show that the function in Eq. (12.103) satisfies the wave equation:

$$\left(\frac{\partial^2 y}{\partial t^2}\right) = c^2\left(\frac{\partial^2 y}{\partial x^2}\right),$$
$$\left(\frac{\partial^2 y}{\partial t^2}\right) = -A(kc)^2\sin\left[k(x-ct)\right],$$
$$c^2\left(\frac{\partial^2 y}{\partial x^2}\right) = -Ac^2k^2\sin\left[k(x-ct)\right].$$

We can show that the function of Eq. (12.103) represents a traveling wave by showing that a node in the wave moves along the string. When $t=0$, there is a node at $x=0$. At a later time, this node is located at a value of x such that $k(x-ct)$ is still equal to zero. At a time t, $x = ct$ at the node, so that the speed of the wave is equal to c. Using Eq. (14) of Appendix B, we can show that

$$A\sin\left[k\left(x-ct\right)\right] = A\left[\sin\left(kx\right)\cos\left(kct\right) - \cos\left(kx\right)\sin\left(kct\right)\right]. \tag{12.104}$$

This equation exhibits the fact that a traveling wave is equivalent to the sum of two standing waves that interfere with each other constructively and destructively.

Exercise 12.16. Find the speed of propagation of a traveling wave in an infinite string with the same mass per unit length and the same tension force as the violin string in the previous exercise.

12.7.3 The Schrödinger Equation

The time-dependent Schrödinger equation for a particle moving only in the x direction is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}+\mathcal{V}(x)\Psi=i\hbar\frac{\partial\Psi}{\partial t}, \tag{12.105}$$

where $\hbar = h/2\pi$, where h is Planck's constant, equal to $6.6260755 \times 10^{-34}$ J s, and where $\mathcal{V}(x)$ represents the potential energy. We separate the variables by assuming the product wave function

$$\Psi(x,t)=\psi(x)\theta(t). \tag{12.106}$$

Substitution of this trial solution into the differential equation gives

$$-\frac{\hbar^2}{2m}\theta(t)\frac{\partial^2\psi}{\partial x^2}+\mathcal{V}(x)\theta(t)\psi(x)=i\hbar\psi(x)\frac{\partial\theta}{\partial t}. \tag{12.107}$$

Division by $\psi(x)\theta(t)$ separates the variables:

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi}{\partial x^2}+\mathcal{V}(x)\psi(x)=i\hbar\frac{1}{\theta(t)}\frac{\partial\theta}{\partial t}. \tag{12.108}$$

Each side of this equation must be a constant function of its independent variable, which we denote by E:

$$\frac{\partial^2\psi}{\partial x^2}=-\frac{2m(E-\mathcal{V}\propto}{\hbar^2}\psi, \tag{12.109}$$

$$\frac{\partial\theta}{\partial t}=-\frac{iE}{\hbar}\theta. \tag{12.110}$$

Both of these equations are similar to the equation that we solved for the flexible string. Equation (12.109) can be rewritten

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+\mathcal{V}(x)\psi=E\psi. \tag{12.111}$$

This is the *time-independent Schrödinger equation* for motion in the x direction. It is called an *eigenvalue equation*, and the quantity E is called the *eigenvalue* . This eigenvalue E is a possible value of the energy. In many cases, the boundary conditions impose conditions such that E can take on only specific discrete values, and we say that the energy is *quantized*.

12.8 SOLUTION OF DIFFERENTIAL EQUATIONS USING LAPLACE TRANSFORMS

Some differential equations can be solved by taking the Laplace transforms of the terms in the equation, applying some of the theorems presented in Section 11.3 to obtain an expression for the Laplace transform of the unknown function, and then finding the inverse transform. We illustrate this procedure with the differential equation for the less than critically damped harmonic oscillator,[6] Eq. (12.43), which can be rewritten

$$\left(\frac{\mathrm{d}^2z}{\mathrm{d}t^2}\right)+\frac{\zeta}{m}\frac{\mathrm{d}z}{\mathrm{d}t}+\frac{k}{m}z=z^{(2)}+\frac{\zeta}{m}z^{(1)}+\frac{k}{m}z=0, \tag{12.112}$$

where we use the notation $z^{(2)}$ for the second derivative $\mathrm{d}^2z/\mathrm{d}t^2$ and $z^{(1)}$ for the first derivative $\mathrm{d}z/\mathrm{d}t$. We take the Laplace transforms of the terms this equation, applying Eq. (11.48) and the $n=2$ version of Eq. (11.49), to express the Laplace transforms of the first and second derivatives. We let $Z(s)$ be the Laplace transform of z and obtain the algebraic equation

$$s^2Z-sz(0)-z^{(1)}(0)+\frac{\zeta}{m}[sZ-z(0)]+\frac{k}{m}Z=0. \tag{12.113}$$

We solve this equation for Z:

$$Z=\frac{sz(0)+z^{(1)}(0)+(\zeta/m)z(0)}{s^2+(\zeta/m)s+k/m}. \tag{12.114}$$

When we find the inverse transform of Z, we will have our answer. In order to match an expression for a transform in Table 11.1, we complete the square in the denominator. (That is, we add a term so that we have a perfect square plus another term:)

$$Z=\frac{sz(0)+z^{(1)}(0)+(\zeta/m)z(0)}{s^2+(\zeta/m)s+\zeta^2/4m^2-\zeta^2/4m^2+k/m} \tag{12.115}$$

$$=\frac{z(0)(s+\zeta/m)+z^{(1)}(0)}{(s+\zeta/2m)^2-\zeta^2/4m^2+k/m}. \tag{12.116}$$

[6] Erwin Kreyszig, *Advanced Engineering Mathematics*, 3rd ed., pp. 156–157, Wiley, New York, 1972.

We have also expressed the numerator in terms of the quantity that is squared in the denominator. We now make the substitutions,

$$a = \frac{\zeta}{2m} \quad \text{and} \quad \omega^2 = \frac{k}{m} - \frac{\zeta^2}{4m^2} = \frac{k}{m} - a^2,$$

so that Eq. (12.115) can be written

$$\begin{aligned} Z &= \frac{z(0)(s+a)}{(s+a)^2+\omega^2} + \frac{z^{(1)}(0)}{(s+a)^2+\omega^2} \\ &= \frac{z(0)(s+a)}{(s+a)^2+\omega^2} + \frac{az(0)+z^{(1)}(0)}{(s+a)^2+\omega^2}. \end{aligned} \quad (12.117)$$

We assume the case of less than critical damping, so that ω^2 is positive.

From Table 11.1, we have the inverse transforms,

$$\mathcal{L}^{-1}\left\{\frac{s}{s^2+\omega^2}\right\} = \cos(\omega t),$$
$$\mathcal{L}^{-1}\left\{\frac{\omega}{s^2+\omega^2}\right\} = \sin(\omega t)$$

and from the shifting theorem of Eq. (11.47)

$$\mathcal{L}\left\{e^{-at}f(t)\right\} = F(s+a), \quad (12.118)$$

so that

$$z(t) = \left[z(0)\cos(\omega t) + \frac{z^{(1)}(0)+az(0)}{\omega}\sin(\omega t)\right]e^{-at}. \quad (12.119)$$

Except for the symbols used for constants, this agrees with the solution obtained earlier in the chapter.

Exercise 12.17. Obtain the solution of Eq. (12.112) in the case of critical damping, using Laplace transforms.

Our discussion of the Laplace transform method for solving differential equations suffices only to introduce the method. The book by Kreyszig in the list at the end of the book is recommended for further study.

12.9 NUMERICAL SOLUTION OF DIFFERENTIAL EQUATIONS

Many differential equations occur for which no solution can be obtained with pencil and paper. With the use of programmable computers, it is now frequently possible to obtain numerical approximations to the solutions of these equations to any desired degree of accuracy.

12.9.1 Euler's Method

Euler's method is simple to understand and implement, but it is not very accurate. Consider a differential equation for a variable x as a function of t that can be schematically represented by

$$\frac{dx}{dt} = f(x,t) \quad (12.120)$$

with the initial condition that $x(0) = x_0$, a known value. A *formal solution* can be written

$$x(t') = x_0 + \int_0^{t'} f(x,t)dt. \quad (12.121)$$

Like any other formal solution, this cannot be used in practice, since the variable x in the integrand function depends on t in some way that we do not yet know.

Euler's method assumes that if t' is small enough, the integrand function in Eq. (12.121) can be replaced by its value at the beginning of the integration. We replace t' by the symbol Δt and write

$$x(\Delta t) \approx x_0 + \int_0^{\Delta t} f(x_0,0)dt = x_0 + f(x_0,0)\Delta t. \quad (12.122)$$

A small value of Δt is chosen, and this process is repeated until the desired value of t' is reached. Let x_i be the value of x obtained after carrying out the process i times, and let t_i equal $i\Delta t$, the value of t after carrying out the process i times. We write

$$x_{i+1} \approx x_i + \Delta t f(x_i,t_i). \quad (12.123)$$

Euler's method is analogous to approximating an integral by the area under a bar graph, except that the height of each bar is obtained by starting with the approximate height of the previous bar and using the known slope of the tangent line.

Example 12.13. The differential equation for a first-order chemical reaction without back reaction is

$$\frac{dc}{dt} = -kc,$$

where c is the concentration of the single reactant and k is the rate constant. Set up an Excel spreadsheet to carry out Euler's method for this differential equation. Carry out the calculation for the initial concentration 1.000 mol l^{-1}, $k =$ 1.000 s^{-1} for a time of 2.000 s and $\Delta t = 0.100$ s.

Here are the numbers from the spreadsheet, using:

Time	Concentration
0.0	1
0.1	0.9
0.2	0.81
0.3	0.729
0.4	0.6561
0.5	0.59049
0.6	0.531441
0.7	0.4782969
0.8	0.43046721
0.9	0.387420489
1.0	0.34867844
1.1	0.313810596
1.2	0.282429536
1.3	0.254186583
1.4	0.228767925
1.5	0.205891132
1.6	0.185302019
1.7	0.166771817
1.8	0.150094635
1.9	0.135085172
2.0	0.121576655

The result of the spreadsheet calculation is

$$c(2.00\text{ s}) \approx 0.1216\text{ mol l}^{-1}$$

The correct answer is

$$\begin{aligned} c(2.00\text{ s}) &= c(0)e^{-kt} \\ &= (1.000\text{ mol l}^{-1}) \\ &\quad \times \exp\left[-(1.000\text{ s}^{-1})\,(2.000\text{ s})\right] \\ &= 0.1353\text{ mol l}^{-1} \end{aligned}$$

Using a value of $\Delta t = 0.05$ s, the result of the spreadsheet calculation is

$$c(2.00\text{ s}) \approx 0.1258\text{ mol l}^{-1}$$

Exercise 12.18. The differential equation for a second-order chemical reaction without back reaction is

$$\frac{dc}{dt} = -kc^2,$$

where c is the concentration of the single reactant and k is the rate constant. Set up an Excel spreadsheet to carry out Euler's method for this differential equation. Carry out the calculation for the initial concentration 1.000 mol l^{-1}, $k = 1.000$ l mol^{-1} s^{-1} for a time of 2.000 s and for $\Delta t = 0.100$ s. Compare your result with the correct answer.

12.9.2 The Runge–Kutta Method

Since Euler's method is not accurate except for very small values of Δt, more sophisticated methods have been devised. One such widely used method is the *Runge–Kutta method*, which is somewhat analogous to using Simpson's method for a numerical integration, as discussed in Chapter 7.[7]

Consider again the differential equation represented by

$$\frac{dx}{dt} = f(x,t).$$

In the Runge–Kutta method, Eq. (12.123) is replaced by

$$x_{i+1} \approx x_i + \frac{1}{6}(F_1 + 2F_2 + 2F_3 + F_4), \qquad (12.124)$$

where

$$F_1 = \Delta t f(x_i, t_i), \qquad (12.125)$$

$$F_2 = \Delta t f\left(x_i + \frac{1}{2}F_1, t_i + \frac{\Delta t}{2}\right), \qquad (12.126)$$

$$F_3 = \Delta t f\left(x_i + \frac{1}{2}F_2, t_i + \frac{\Delta t}{2}\right), \qquad (12.127)$$

$$F_4 = \Delta t f\left(x_i + F_3, t_i + \Delta t\right). \qquad (12.128)$$

We do not present the derivation of this method, which is discussed in the book by Burden and Faires listed at the end of the book.

There are also other numerical methods for solving differential equations, which we do not discuss. The numerical methods can be extended to sets of simultaneous differential equations such as those that occur in the analysis of chemical reaction mechanisms. Many of these sets of equations have a property called *stiffness* that makes them difficult to treat numerically. Techniques have been devised to handle this problem, which is beyond the scope of this book.[8]

12.9.3 Solution of Differential Equations with Mathematica

Mathematica can solve differential equations both symbolically and numerically.

[7] See the book by Burden, Faires, and Reynolds and the book by Hornbeck listed at the end of the book.

[8] C. J. Aro, *Comput. Phys. Comm.* **97**, 304 (1996).

Symbolic Solution

The statement *DSolve* is used to carry out a symbolic solution of a differential equation. We illustrate this with an example.

Example 12.14. Use Mathematica to solve the differential equation

$$\frac{dy}{dx} = ay(x).$$

We enter the Mathematica statement

DSolve[y'[x]= =a y[x], y[x], x]

and press the "Enter" key. Notice how the statement is written inside the brackets. First comes the equation, with the first derivative denoted by y'. The double equal sign must be used to let Mathematica know that an equation is to be solved. We have used a blank space between the a and the y[x] to indicate multiplication. After a comma comes the specification of the dependent variable, y[x]. Note the use of brackets, not parentheses. The independent variable must be included inside the brackets. After another comma comes the statement of the independent variable. Mathematica returns the output

Out[1]={{y[x] → $e^{a\,x}$ C[1]}}

Note the space between the a and the x and the space between the exponential and the constant C[1] in the output. The constant C[1] is to be determined by initial conditions. An initial condition can be included in the original input statement. For example, if $y(0) = 2$, we would enter

DSolve[{y'[x]==a y[x],y[0]==2},y[x],x]

and press the "Enter" key or a "Shift-Return." The output would be

Out[1]={{y[x] → 2 $e^{a\,x}$}}

Numerical Solution

Mathematica carries out numerical solutions of differential equation for which no exact solution can be written. The solution is given in terms of an interpolating function, which is a table of values of the unknown function for different values of the independent variable. The program finds a numerical value of the function for a specific value of the independent variable by interpolation in this table. The statement *NDSolve* is used to solve the differential equation, as in the next example:

Example 12.15. Obtain the numerical solution to the differential equation

$$\frac{dy}{dx} = 2\sin(x)$$

for the interval $0 < x < \pi$ with the initial condition $y(0) = 1$.

We type the input

NDSolve[{y'[x]==2 sin[x], y[0]==1}, y, {x, 0, Pi}]

and press the "Enter" key. The output appears

Out[1]={{y → InterpolatingFunction[{0,3.141593},<
>]}}

To obtain the value of the function at some value of x, say $x = 2$, we type the input

y[2] /.%1

and press the "Enter" key or a "Shift-return". The /. is the replacement operator in Mathematica and is typed as two characters, a forward slash and a period. The %1 means that the output line number 1 is referred to. If the interpolating function had been in line 3, we would have typed %3. The output result now appears

Out[2]={3.83229}

To obtain a graph of the solution, we enter

Plot[Evaluate[y[x] /. %1], {x, 0, Pi}]

and press the "Enter" key or a "Shift-Return". The graph appears as the output.

PROBLEMS

1. An object moves through a fluid in the x direction. The only force acting on the object is a frictional force that is proportional to the negative of the velocity:

$$F_x = -\zeta v_x = -\zeta\left(\frac{dx}{dt}\right).$$

Write the equation of motion of the object. Find the general solution to this equation and obtain the particular solution that applies if $x(0) = 0$ and $v_x(0) = v_0 =$ constant. Construct a graph of the position as a function of time.

2. A particle moves along the z axis. It is acted upon by a constant gravitational force equal to $-\mathbf{k}mg$, where $\mathbf{k}$ is the unit vector in the z direction. It is also acted on by a frictional force given by

$$\mathbf{F}_f = -\mathbf{k}\zeta\left(\frac{dz}{dt}\right),$$

where ζ is a constant called a "friction constant." Find the equation of motion and obtain a general solution. Find z as a function of time if $z(0) = 0$ and $v_x(0) = 0$. Draw a graph of z as a function of time.

3. An object sliding on a solid surface experiences a frictional force that is constant and in the opposite direction to the velocity if the particle is moving, and is zero it is not moving. Find the position of the particle as a function of time if it moves only in the x direction and the initial position is $x(0) = 0$ and the initial velocity is $v_x(0) = v_0 =$ constant. Proceed as though the constant force were present at all times and then cut the solution off at the point at which the velocity vanishes. That is, just say that the particle is fixed after this time. Construct a graph of x as a function of time for the case that $v_0 = 10.00\ \text{m s}^{-1}$.

4. A harmonic oscillator has a mass $m = 0.300$ kg and a force constant $k = 155\ \text{N m}^{-1}$:

- **(a)** Find the period and the frequency of oscillation.
- **(b)** Find the value of the friction constant ζ necessary to produce critical damping with this oscillator. Find the value of the constant λ_1.
- **(c)** Construct a graph of the position of the oscillator as a function of t for the initial conditions $z(0) = 0, v_z(0) = 0.100\ \text{m s}^{-1}$.

5. A less than critically damped harmonic oscillator has a mass $m = 0.3000$ kg, a force constant $k = 98.00\ \text{N m}^{-1}$, and a friction constant $\zeta = 1.000\ \text{kg s}^{-1}$.

- **(a)** Find the circular frequency of oscillation ω and compare it with the frequency that would occur if there were no damping.
- **(b)** Find the time required for the real exponential factor in the solution to drop to one-half of its value at $t = 0$.

6. A forced harmonic oscillator with a circular frequency $\omega = 6.283\ \text{s}^{-1}$ (frequency $\nu = 1.000\ \text{s}^{-1}$) is exposed to an external force $F_0 \sin(\alpha t)$ with circular frequency $\alpha = 7.540\ \text{s}^{-1}$ such that in the solution of Eq. (12.63) becomes

$$z(t) = \sin(\omega t) + 0.100 \sin\left(\alpha t\right).$$

Using Excel or Mathematica, make a graph of $z(t)$ for a time period of at least 20 s.

7. A forced harmonic oscillator with mass $m = 0.300$ kg and a circular frequency $\omega = 6.283\ \text{s}^{-1}$ (frequency $\nu = 1.000\ \text{s}^{-1}$) is exposed to an external force $F_0 \exp(-\beta t) \sin(\alpha t)$ with $\alpha = 7.540\ \text{s}^{-1}$ and $\beta = 0.500\ \text{s}^{-1}$. Find the solution to its equation of motion. Construct a graph of the motion for several values of F_0.

8. A tank contains a solution that is rapidly stirred, so that it remains uniform at all times. A solution of the same solute is flowing into the tank at a fixed rate of flow, and an overflow pipe allows solution from the tank to flow out at the same rate. If the solution flowing in has a fixed concentration that is different from the initial concentration in the tank, write and solve the differential equation that governs the number of moles of solute in the tank. The inlet pipe allows A moles per hour to flow in and the overflow pipe allows Bn moles per hour to flow out, where A and B are constants and n is the number of moles of solute in the tank. Find the values of A and B that correspond to a volume in the tank of 100.0 l, an input of $1.000\ \text{l h}^{-1}$ of a solution with $1.000\ \text{mol l}^{-1}$, and an output of $1.000\ \text{l h}^{-1}$ of the solution in the tank. Find the concentration in the tank after 5.00 h, if the initial concentration is zero.

9. An nth-order chemical reaction with one reactant obeys the differential equation

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -kc^n,$$

where c is the concentration of the reactant and k is a constant. Solve this differential equation by separation of variables. If the initial concentration is c_0 moles per liter, find an expression for the time required for half of the reactant to react.

10. Find the solution to the differential equation

$$\frac{\mathrm{d}^2y}{\mathrm{d}x^2} - \frac{\mathrm{d}y}{\mathrm{d}x} - 2y = -xe^x.$$

11. Test the following equations for exactness and solve the exact equations:

- **(a)** $(x^2 + xy + y^2)\mathrm{d}x + \left(4x^2 - 2xy + 3y^2\right)\mathrm{d}y = 0.$
- **(b)** $ye^x\mathrm{d}x + e^x\mathrm{d}y = 0.$
- **(c)** $\left[2xy - \cos(x)\right]\mathrm{d}x + \left(x^2 - 1\right)\mathrm{d}y = 0.$

12. Use Mathematica to solve the differential equation symbolically

$$\frac{\mathrm{d}y}{\mathrm{d}x} + y\cos(x) = e^{-\sin(x)}.$$

13. Use Mathematica to obtain a numerical solution to the differential equation in the previous problem for the range $0 < x < 10$ and for the initial condition $y(0) = 1$. Evaluate the interpolating function for several values of x and make a plot of the interpolating function for the range $0 < x < 10$.

14. Solve the differential equation

$$\frac{\mathrm{d}^2y}{\mathrm{d}x^2} - 4y = 2e^{3x} + \sin(x).$$

15. Radioactive nuclei decay according to the same differential equation which governs first-order chemical reactions, Eq. (12.71). In living matter, the isotope ^{14}C is continually replaced as it decays, but it decays without replacement beginning with the death of the organism. The half-life of the isotope (the time required for half of

an initial sample to decay) is 5730 years. If a sample of charcoal from an archaeological specimen exhibits 0.97 disintegrations of ^{14}C per gram of carbon per minute and wood recently taken from a living tree exhibits 15.3 disintegrations of ^{14}C per gram of carbon per minute, estimate the age of the charcoal.

16. A pendulum of length L oscillates in a vertical plane. Assuming that the mass of the pendulum is all concentrated at the end of the pendulum, show that it obeys the differential equation

$$L\left(\frac{d^2\phi}{dt^2}\right) = -g\sin(\phi),$$

where g is the acceleration due to gravity and ϕ is the angle between the pendulum and the vertical. This equation cannot be solved exactly. For small oscillations such that

$$\sin(\phi) \approx \phi,$$

find the solution to the equation. What is the period of the motion? What is the frequency? Find the value of L such that the period equals 2.000 s.

17. Use Mathematica to obtain a numerical solution to the pendulum equation in the previous problem without approximation for the case that $L = 1.000$ m with the initial conditions $\phi(0) = 0.350$ rad (about 20°) and $d\phi/dt = 0$. Evaluate the solution for $t = 0.500$ s, 1.000 s, and 1.500 s. Make a graph of your solution for $0 < t < 4.00$ s. Repeat your solution for $\phi(0) = 0.050$ rad (about 2.9°) and $d\phi/dt = 0$. Determine the period and the frequency from your graphs. How do they compare with the solution from the previous problem?

18. Obtain the solution for Eq. (12.62) for the forced harmonic oscillator using Laplace transforms.

19. An object of mass m is subjected to an oscillating force in the x direction given by $F_0\sin(bt)$ where a and b are constants. Find the solution to the equation of motion of the particle. Find the particular solution for the case that $x(0) = 0$ and $dx/dt = 0$ at $t = 0$.

20. An object of mass m is subjected to a gradually increasing force given by $F_0(1-e^{-bt})$ where a and b are constants. Solve the equation of motion of the particle. Find the particular solution for the case that $x(0) = 0$ and $dx/dt = 0$ at $t = 0$.

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Chapter 13

Operators, Matrices, and Group Theory

Principal Facts and Ideas

- An operator is a symbol that stands for one or more mathematical operations.
- If an operator $\widehat{A}$ operates on a function f, the result is a new function, g: $\widehat{A}f = g$.
- Operator algebra manipulates operator symbols according to rules that are slightly different from those of ordinary algebra. One difference is that operator multiplication is not necessarily commutative, and another is that division by an operator is not defined.
- An eigenvalue equation has the form $\widehat{A}f = af$ where f is an eigenfunction and a is an eigenvalue.
- Symmetry operators move points in space relative to a symmetry element. If a symmetry operator belongs to a symmetrical object, it leaves that object in the same conformation after operating on all particles of the object.
- Symmetry operators can operate on functions as well as on points and can have eigenfunctions with eigenvalues equal to 1 or to -1. An electronic wave function of a molecule can be an eigenfunction of the symmetry operators which belong to the nuclear framework of a molecule.
- A matrix is a list of quantities, arranged in rows and columns.
- Matrices can be manipulated according to the rules of matrix algebra, which are similar to the rules of operator algebra.
- The inverse of a matrix obeys $\mathbf{A}^{-1}\mathbf{A} = \mathbf{A}\mathbf{A}^{-1} = \mathbf{E}$ where $\mathbf{E}$ is the identity matrix. The inverse of a given matrix can be obtained by the Gauss-Jordan elimination procedure.
- A group is a set of elements obeying certain conditions, with a single operation combining two elements to give a third element of the group. This operation is called multiplication and is noncommutative.
- The symmetry operators belonging to a symmetrical object form a group.
- A set of matrices obeying the same multiplication table as a group is a representation of the group.
- Various theorems of group theory are useful in studying the symmetry properties of molecules.

Objectives

After studying this chapter, you should be able to:

- perform the elementary operations of operator algebra;
- identify and use symmetry operators associated with a symmetrical molecule;
- perform the elementary operations of matrix algebra, including matrix multiplication and finding the inverse of a matrix;
- identify a group of symmetry operators and construct a multiplication table for the group;
- assign the proper symmetry group to a given molecule in its equilibrium conformation.

13.1 MATHEMATICAL OPERATORS

A *mathematical operator* is a symbol that stands for carrying out one or more mathematical operations on some function. For example, we can use the symbol d/dx to stand for the operation of differentiating with respect to x. When an operator operates on a function, the result is generally another function. We will usually assign a symbol to an operator that consists of a letter with a caret (ˆ) over it. We will discuss three types of operators:

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1. *Multiplication operators* are operators that stand for multiplying a function either by a constant or by another function.
2. *Derivative operators* stand for differentiating a function one or more times with respect to one or more independent variables.
3. *Symmetry operators* are defined by the way they move a point in space but can also operate on functions.

Example 13.1. For the operator

$$\widehat{A} = x + \frac{\mathrm{d}}{\mathrm{d}x}$$

find $\widehat{A}f$ if $f = a\sin(bx)$, where a and b are constants.

$$\begin{aligned}\widehat{A}a\sin(bx) &= \left(x + \frac{\mathrm{d}}{\mathrm{d}x}\right) a\sin(bx)\\ &= xa\sin(bx) + ab\cos(bx).\end{aligned}$$

13.1.1 Eigenfunctions and Eigenvalues

If the result of operating on a function with an operator is a function that is proportional to the original function, the function is called an *eigenfunction* of that operator, and the proportionality constant is called an *eigenvalue*.[1] If $\widehat{A}$ is an operator that can operate on a function f such that

$$\boxed{\widehat{A}f = af} \tag{13.1}$$

then f is an eigenfunction of $\widehat{A}$ and a is the eigenvalue corresponding to that eigenfunction. An equation like Eq. (13.1) is called an *eigenvalue equation*. The time-independent Schrödinger equation of quantum mechanics is an eigenvalue equation, and other eigenvalue equations are also important in quantum mechanics.

Example 13.2. Find the eigenfunctions and eigenvalues for the operator $\mathrm{d}^2/\mathrm{d}x^2$.

We need to find a function $f(x)$ and a constant b such that

$$\frac{\mathrm{d}^2 f}{\mathrm{d}x^2} = bf.$$

A trial solution that will work is

$$f = e^{\lambda t}.$$

Substitution of this trial solution into the differential equation gives

$$\frac{\mathrm{d}^2 e^{\lambda t}}{\mathrm{d}x^2} = \lambda^2 e^{\lambda t} = b\, e^{\lambda t}.$$

The characteristic equation is

$$\begin{aligned}\lambda^2 &= b,\\ \lambda &= \pm\sqrt{b}.\end{aligned}$$

The general solution to the differential equation is

$$f(x) = A\exp\left(\sqrt{b}x\right) + B\exp\left(-\sqrt{b}x\right),$$

where A and B are constants. Each of the two terms is an eigenfunction, so we write

$$\begin{aligned}f_1(x) &= A\exp\left(\sqrt{b}x\right),\\ f_2(x) &= B\exp\left(-\sqrt{b}x\right).\end{aligned}$$

The two eigenfunctions correspond to the same eigenvalue, equal to b. Since no boundary conditions were stated, the eigenvalue can take on any value, as can the constants A and B.

Exercise 13.1. Find the eigenfunctions and eigenvalues of the operator $i\dfrac{\mathrm{d}}{\mathrm{d}x}$, where $i = \sqrt{-1}$.

13.1.2 Operator Algebra

Although a mathematical operator is a symbol that stands for the carrying out of an operation, an operator algebra exists in which we manipulate the operator symbols much as we manipulate numbers and symbols in ordinary algebra. We will sometimes write *operator equations* in which the operators occur without explicit mention of the functions on which they operate. We define the *sum of two operators:* If we write the operator equation

$$\widehat{C} = \widehat{A} + \widehat{B} \tag{13.2}$$

then

$$\widehat{C}f = (\widehat{A} + \widehat{B})f = \widehat{A}f + \widehat{B}f, \tag{13.3}$$

where $\widehat{A}$ and $\widehat{B}$ are two operators and where f is a function on which $\widehat{A}$ and $\widehat{B}$ can operate.

The *product of two operators* is defined as the successive operation of the operators, with the one on the right operating first. If we write the operator equation

$$\widehat{C} = \widehat{A}\widehat{B} \tag{13.4}$$

then

$$\widehat{C}f = \widehat{A}(\widehat{B}f). \tag{13.5}$$

The result of $\widehat{B}$ operating on f is in turn operated on by $\widehat{A}$ and the result is said to equal the result of operating on f with the product $\widehat{A}\widehat{B}$.

[1] The word "eigenvalue" is a partial translation of the German *Eigenwert*, sometimes translated as "characteristic value." The word *eigenfunction* is a partial translation of the German *Eigenfunktion*, sometimes translated as "characteristic function."

Example 13.3. Find the operator equal to the operator product $\frac{\mathrm{d}}{\mathrm{d}x}\hat{x}$.

We take an arbitrary differentiable function $f = f(x)$ and apply the operator product to it,

$$\frac{\mathrm{d}}{\mathrm{d}x}\hat{x}f = x\frac{\mathrm{d}f}{\mathrm{d}x} + f\frac{\mathrm{d}x}{\mathrm{d}x} = \left(x\frac{\mathrm{d}}{\mathrm{d}x} + \widehat{E}\right)f,$$

where $\widehat{E}$ is the identity operator, defined to be the operator for multiplication by unity (same as doing nothing). The symbol $\widehat{E}$ is chosen from the German word "Einheit," meaning "unity." The operator equation that is equivalent to this equation is

$$\frac{\mathrm{d}}{\mathrm{d}x}\hat{x} = x\frac{\mathrm{d}}{\mathrm{d}x} + \widehat{E}.$$

As in this example we will usually omit the caret symbol over a multiplication operator.

Exercise 13.2. Find the operator equal to the operator product $\frac{\mathrm{d}^2}{\mathrm{d}x^2}x$.

The *difference of two operators* is given by

$$(\widehat{A} - \widehat{B}) = \widehat{A} + (-\widehat{E})\widehat{B}. \tag{13.6}$$

Operator multiplication is *associative*. This means that if $\widehat{A}$, $\widehat{B}$, and $\widehat{C}$ are operators, then

$$\boxed{(\widehat{A}\,\widehat{B})\widehat{C} = \widehat{A}(\widehat{B}\widehat{C})}. \tag{13.7}$$

Operator multiplication and addition are *distributive*. This means that if $\widehat{A}$, $\widehat{B}$, and $\widehat{C}$ are operators.

$$\boxed{\widehat{A}(\widehat{B} + \widehat{C}) = \widehat{A}\widehat{B} + \widehat{A}\widehat{C}}. \tag{13.8}$$

Operator multiplication is not necessarily *commutative*. This means that in some cases the same result is not obtained if the sequence of operation of two operators is reversed:

$$\boxed{\widehat{A}\widehat{B} \neq \widehat{B}\widehat{A} \quad \text{(possible)}}. \tag{13.9}$$

If the operator $\widehat{A}\widehat{B}$ is equal to the operator $\widehat{B}\widehat{A}$ then $\widehat{A}$ and $\widehat{B}$ are said to *commute*. The *commutator* of $\widehat{A}$ and $\widehat{B}$ is denoted by $\left[\widehat{A},\widehat{B}\right]$and defined by

$$\boxed{\left[\widehat{A},\widehat{B}\right] = \widehat{A}\widehat{B} - \widehat{B}\widehat{A} \quad \text{(definition of the commutator)}}. \tag{13.10}$$

If $\widehat{A}$ and $\widehat{B}$ commute, then $\left[\widehat{A},\widehat{B}\right] = \hat{0}$, where $\hat{0}$ is the *null operator*, equivalent to multiplying by zero.

Example 13.4. Find the commutator $\left[\frac{\mathrm{d}}{\mathrm{d}x}, x\right]$.

We apply the commutator to an arbitrary differentiable function $f(x)$:

$$\left[\frac{\mathrm{d}}{\mathrm{d}x}, x\right]f = \frac{\mathrm{d}}{\mathrm{d}x}(xf) - x\frac{\mathrm{d}f}{\mathrm{d}x} = x\frac{\mathrm{d}f}{\mathrm{d}x} + f - x\frac{\mathrm{d}f}{\mathrm{d}x} = f. \tag{13.11}$$

Therefore,

$$\left[\frac{\mathrm{d}}{\mathrm{d}x}, x\right] = \widehat{E}. \tag{13.12}$$

Exercise 13.3. Find the commutator $[x^2, \frac{\mathrm{d}^2}{\mathrm{d}x^2}]$.

Here are a few facts that will generally predict whether two operators will commute:

- An operator containing a multiplication by a function of x and one containing d/dx will generally not commute.
- Two multiplication operators commute. If g and h are functions of the same or different independent variables or are constants, then

$$[\hat{g},\hat{h}] = 0. \tag{13.13}$$

- Operators acting on different independent variables commute. For example,

$$\left[x\frac{\mathrm{d}}{\mathrm{d}x}, \frac{\mathrm{d}}{\mathrm{d}y}\right] = 0. \tag{13.14}$$

- An operator for multiplication by a constant commutes with any other operator.

An operator raised to the nth power stands for n successive applications of the operator:

$$\boxed{\widehat{A}^n = \widehat{A}\widehat{A}\widehat{A}\cdots\widehat{A} \quad (n \text{ factors})}. \tag{13.15}$$

Example 13.5. If $\widehat{A} = x + \frac{\mathrm{d}}{\mathrm{d}x}$, find $\widehat{A}^2$.

$$\begin{aligned}\widehat{A}^2 &= \left(x + \frac{\mathrm{d}}{\mathrm{d}x}\right)\left(x + \frac{\mathrm{d}}{\mathrm{d}x}\right),\\ &= \left(x^2 + \frac{\mathrm{d}}{\mathrm{d}x}x + x\frac{\mathrm{d}}{\mathrm{d}x} + \frac{\mathrm{d}^2}{\mathrm{d}x^2}\right).\end{aligned}$$

The order of the factors in each term must be maintained because the two terms in the operator do not commute with each other.

Exercise 13.4. If $\widehat{A} = x + \frac{\mathrm{d}}{\mathrm{d}x}$, find $\widehat{A}^3$.

Example 13.6. For the operator $\widehat{A} = x + \frac{\mathrm{d}}{\mathrm{d}x}$, find $\widehat{A}^2 f$ if $f(x) = \sin(ax)$.

$$\begin{aligned}&\left(x^2 + \frac{\mathrm{d}}{\mathrm{d}x}x + x\frac{\mathrm{d}}{\mathrm{d}x} + \frac{\mathrm{d}^2}{\mathrm{d}x^2}\right)\sin(ax)\\ &= x^2\sin(ax) + \sin(ax) + xa\cos(ax)\\ &\quad + xa\cos(ax) - a^2\sin(ax),\\ &= x^2\sin(ax) + \sin(ax) + 2xa\cos(ax) - a^2\sin(ax).\end{aligned}$$

Exercise 13.5. Find an expression for $\widehat{B}^2$ if $\widehat{B} = x(\mathrm{d}/\mathrm{d}x)$ and find $\widehat{B}^2 f$ if $f = bx^4$.

Division by an operator is not defined. However, we define the *inverse of an operator* as the operator that "undoes" what the first operator does. The inverse of $\widehat{A}$ is denoted by $\widehat{A}^{-1}$:

$$\boxed{\widehat{A}\widehat{A}^{-1} = \widehat{A}^{-1}\widehat{A} = \widehat{E}}. \tag{13.16}$$

Note that $\widehat{A}$ is also the inverse of $\widehat{A}^{-1}$.

$$\widehat{A}\widehat{A}^{-1} f = \boxed{\widehat{A}^{-1}\widehat{A} f = \widehat{E} f = f}. \tag{13.17}$$

Not all operators possess inverses. For example, there is no inverse for multiplication by zero.

Operator algebra can be used to solve some differential equations.[2] A linear differential equation with constant coefficients can be written in operator notation and solved by operator algebra.

Example 13.7. Solve the equation

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} - 3\frac{\mathrm{d}y}{\mathrm{d}x} + 2y = 0$$

using operators.

The equation can be written as

$$\left(\widehat{\mathrm{D}}_x^2 - 3\widehat{\mathrm{D}}_x + 2\right) y = 0,$$

where the symbol $\widehat{\mathrm{D}}_x$ stands for $\mathrm{d}/\mathrm{d}x$. The equation can be written as an operator equation:

$$\left(\widehat{\mathrm{D}}_x^2 - 3\widehat{\mathrm{D}}_X + 2\right) = 0.$$

We factor this equation to obtain

$$(\widehat{\mathrm{D}}_x - 2)(\widehat{\mathrm{D}}_x - 1) = 0.$$

The two roots are obtained from

$$\begin{aligned} \widehat{\mathrm{D}}_x - 2 &= 0, \\ \widehat{\mathrm{D}}_x - 1 &= 0. \end{aligned}$$

These equations are the same as

$$\begin{aligned} \frac{\mathrm{d}y}{\mathrm{d}x} - 2y &= 0, \\ \frac{\mathrm{d}y}{\mathrm{d}x} - y &= 0. \end{aligned}$$

The solutions to these equations are

$$\begin{aligned} y &= e^{2x}, \\ y &= e^{x}. \end{aligned}$$

Since both of these must be solutions to the original equation, the general solution is

$$y = c_1 e^{2x} + c_2 e^{x},$$

where c_1 and c_2 are arbitrary constants.

Exercise 13.6. Show that the solution in the previous example satisfies the original equation.

13.1.3 Operators in Quantum Mechanics

One of the postulates of quantum-mechanical theory is that for every mechanical variable there is a corresponding mathematical operator. For example, the operator that corresponds to the mechanical energy is the Hamiltonian operator, and the time-independent Schrödinger equation is the eigenvalue equation for this operator. For motion in the x direction of a single particle of mass m with a potential energy given by $\mathcal{V}(x)$, the Hamiltonian operator is

$$\widehat{H} = -\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2} + \mathcal{V}(x), \tag{13.18}$$

where $\hbar$ stands for Planck's constant divided by 2π. The term $\mathcal{V}(x)$ stands for multiplication by the potential energy function. The operator for the x coordinate is multiplication by x. The operator for the x component of the linear momentum is

$$\widehat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x} \tag{13.19}$$

where i is the imaginary unit, equal to $\sqrt{-1}$.

Example 13.8. Find an eigenfunction of $\widehat{p}_x$.

Denote the eigenfunction by f.

$$\begin{aligned} \widehat{p}_x f &= \frac{\hbar}{i}\frac{\partial f}{\partial x} = af, \\ \frac{\partial f}{\partial x} &= \frac{ia}{\hbar} f, \\ \frac{1}{f}\frac{\partial f}{\partial x} &= \frac{ia}{\hbar}, \\ \ln(f) &= \frac{iax}{\hbar} + C, \\ f &= e^{C} e^{iax/\hbar}, \end{aligned}$$

where C is an arbitrary constant. Since no boundary condition was specified, the eigenvalue a can take on any value.

[2] See, for example, Max Morris and Orley Brown, *Differential Equations*, 3rd ed. pp. 86–89, Prentice-Hall, Englewood Cliffs, NJ, 1952.

Exercise 13.7. Find the eigenfunction of the Hamiltonian operator for motion in the x direction if $\mathcal{V}(x) = E_0 =$ constant.

All of the quantum-mechanical operators are *hermitian*.[3] If an operator, $\widehat{A}$, is hermitian, it obeys the relation

$$\int \chi^* \widehat{A} \psi \, \mathrm{d}q = \int \left(\widehat{A}^* \chi^*\right) \psi \, \mathrm{d}q, \tag{13.20}$$

where q stands for all of the coordinates on which the functions χ and ψ depend. The asterisk (*) stands for taking the complex conjugate. The integrals in this formula must be taken over all of the values of the coordinates, and if the coordinates can become infinite, the integrals must converge.

Example 13.9. Show that the operator d/dx is not hermitian.

We assume that x can range over all real values and integrate by parts:

$$\int_{-\infty}^{\infty} \chi^* \frac{\mathrm{d}\psi}{\mathrm{d}x} \mathrm{d}x = \chi^* \psi \big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{\mathrm{d}\chi^*}{\mathrm{d}x} \psi \, \mathrm{d}x.$$

In order for the integrals to converge, the functions χ and ψ must vanish for infinite values of x, so that

$$\int_{-\infty}^{\infty} \chi^* \frac{\mathrm{d}\psi}{\mathrm{d}x} \mathrm{d}x = -\int_{-\infty}^{\infty} \frac{\mathrm{d}\chi^*}{\mathrm{d}x} \psi \, \mathrm{d}x.$$

This is the negative of what is required, so that the operator is not hermitian.

Exercise 13.8. Show that the operator for the momentum in Eq. (13.19) is hermitian.

13.2 SYMMETRY OPERATORS

Many common objects are said to be symmetrical. The most symmetrical object is a sphere, which looks the same no matter which way it is turned, and which also looks like its mirror image. A cube, although less symmetrical than a sphere, has 24 different orientations in which it looks the same and it also looks like its mirror image. Many biological organisms have approximate *bilateral symmetry*, meaning that the left side looks like a mirror image of the right side. Although molecules are flexible and can distort in various ways, each molecule has an equilibrium conformation (equilibrium set of relative nuclear positions). Each molecule in its equilibrium conformation has symmetry properties, like any other object.

[3] This property is named for Charles Hermite (1822–1901), a famous French mathematician.

Symmetry properties are related to *symmetry operators*. We define symmetry operators in terms of how they move a point in three-dimensional space. We will consider only *point symmetry operators*, a class of symmetry operators that do not move a point if it is located at the origin of coordinates. We denote the position of a point by its Cartesian coordinates. The Cartesian coordinate axes remain fixed as the point moves. The action of a symmetry operator $\widehat{O}$ is specified by writing

$$\widehat{O}(x_1, y_1, z_1) = (x_2, y_2, z_2), \tag{13.21}$$

where x_1, y_1, z_1 are the coordinates of the original location of a point and x_2, y_2, z_2 are the coordinates of the location to which the operator moves the point. We also write this equation symbolically as

$$\widehat{O} P_1 = P_2, \tag{13.22}$$

where we represent a point by the letter P.

Our first symmetry operator is the *identity operator*, which leaves any point in its original location. We denote it by $\widehat{E}$, the same symbol as for the multiplicative identity operator.

$$\widehat{E}(x_1, y_1, z_1) = (x_1, y_1, z_1). \tag{13.23}$$

If $\mathbf{r}_1$ represents the position vector with components (x_1, y_1, z_1), this equation can be written

$$\widehat{E} \mathbf{r}_1 = \mathbf{r}_1. \tag{13.24}$$

For each symmetry operator, we define a *symmetry element*, which is a point, line, or plane relative to which the symmetry operation is performed. The symmetry element is sometimes denoted by the same symbol as the operator, but without the caret (ˆ). If a point is located on the symmetry element for a given symmetry operator, that symmetry operator will not move the point. The symmetry element of any point symmetry operator must include the origin.

The *inversion operator* is denoted by $\widehat{i}$. It moves a point on a line from its original position through the origin to a location at the same distance from the origin as the original position:

$$\boxed{\widehat{i}(x_1, y_1, z_1) = (-x_1, -y_1, -z_1)}. \tag{13.25}$$

or

$$\boxed{\widehat{i} \mathbf{r}_1 = -\mathbf{r}_1}. \tag{13.26}$$

The symmetry element for the inversion operator is the origin and there is only one inversion operator among the point symmetry operators.

A *reflection operator* moves a point on a line perpendicular to a specified plane, through the plane to a location on the other side of the plane at the same distance from the

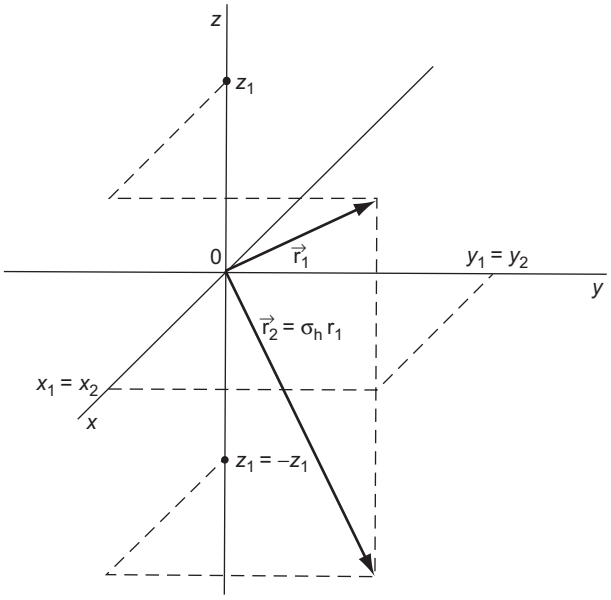

FIGURE 13.1 The action of the reflection operator, $\hat{\sigma}_h$.

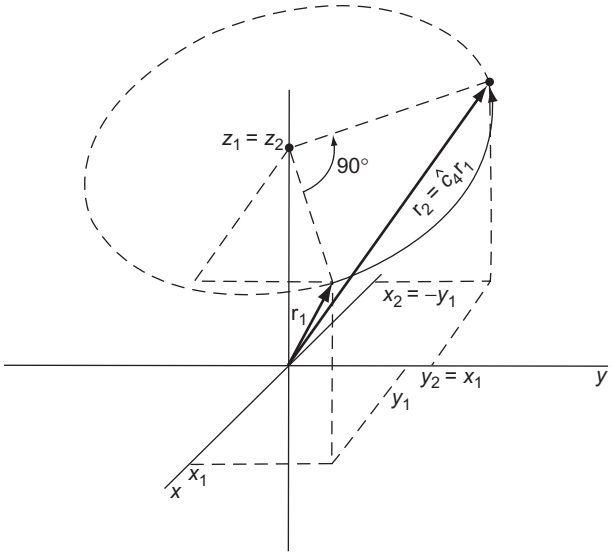

FIGURE 13.2 Action of a rotation operator, $\widehat{C}_4$.

plane as the original point. This motion is called *reflection through the plane*. The specified plane is the symmetry element and must pass through the origin if the operator is a point symmetry operator. There is a different reflection operator for each plane passing through the origin. The operator $\hat{\sigma}_h$ corresponds to reflection through the x–y plane (the h subscript stands for "horizontal" since we regard the z axis as vertical). Figure 13.1 shows the action of the $\hat{\sigma}_h$ operator. There is only one horizontal plane passing through the origin, so there is only one $\hat{\sigma}_h$ operator among the point symmetry operators. The action of $\hat{\sigma}_h$ corresponds to

$$\boxed{\hat{\sigma}_h(x_1,y_1,z_1) = (x_1,y_1,-z_1)}.$$

There are infinitely many reflection operators with vertical symmetry elements, so we must specify the symmetry element. For example, the reflection operator that reflects through the x–z plane could be denoted by $\hat{\sigma}_{v(xz)}$:

$$\hat{\sigma}_{v(xz)}(x_1,y_1,z_1) = (x_1,-y_1,z_1). \tag{13.27}$$

Exercise 13.9. Write an equation similar to Eq. (13.27) for the $\hat{\sigma}_v$ operator whose symmetry element is the y–z plane.

A *rotation operator* moves a point as if it were part of a rigid object rotating about an axis. An ordinary rotation is called a *proper rotation*. The axis of rotation is the symmetry element, and the action of the rotation operator is to move the point along an circle, staying at a fixed perpendicular distance from a fixed point on the axis. The axis of rotation must pass through the origin if the rotation operator is a point symmetry operator. In addition to specifying the axis of rotation, one must specify the direction of rotation and the angle of rotation. By convention, the direction of rotation is taken as counterclockwise when viewed from the positive end of the axis. We consider only angles of rotation such that n applications of the rotation operator produce exactly one complete rotation, where n is a positive integer. Such a rotation operator is denoted by $\widehat{C}_n$. For example, the operator for a rotation of 90° about the z axis is denoted by $\widehat{C}_{4(z)}$.

Figure 13.2 shows the action of the $\widehat{C}_{4(z)}$ operator.

$$\widehat{C}_{4(z)}(x_1,y_1,z_1) = (-y_1,x_1,z_1), \tag{13.28}$$

so that

$$x_2 = -y_1, \quad y_2 = x_1, \quad z_2 = z_1. \tag{13.29}$$

Example 13.10. Find $\widehat{C}_{4(z)}(1,-4,6)$.

$$\widehat{C}_{4(z)}(1,-4,6) = (4,1,6).$$

Exercise 13.10. Find $\widehat{C}_{2(x)}(1,2,-3)$.

An *improper rotation* is equivalent to an ordinary (proper) rotation followed by a reflection through a plane that is perpendicular to the rotation axis. Both the rotation axis and the reflection plane must pass through the origin. The symbol for an improper rotation operator is $\widehat{S}_n$, where the subscript n is the number of applications to achieve one full rotation of 360°. The symmetry element for an improper

rotation is the axis of rotation. The action of the operator for an improper rotation of 90° about the z axis is given by

$$\widehat{S}_{4(z)}(x_1,y_1,z_1) = (-y_1,x_1,-z_1). \tag{13.30}$$

The $\widehat{S}_2$ operator is the same as the inversion operator $\hat{\imath}$, and an $\widehat{S}_1$ operator is the same as a reflection operator.

Example 13.11. Find $\widehat{S}_{4(z)}(1,2,3)$.

$$\widehat{S}_{4(z)}(1,2,3) = (1,2,3).$$

Exercise 13.11. Find $\widehat{S}_{2(y)}(3,4,5)$.

Symmetry operators can operate on a set of points as well as on a single point. They can operate on all of the particles of a solid object or on all of the nuclei of a molecule or on all of the electrons of a molecule. A benzene molecule in its equilibrium conformation has the shape of a regular hexagon. If the center of mass is at the origin, the inversion operator moves each of the carbon nuclei to the original location of another carbon nucleus and each of the hydrogen nuclei to the original location of another hydrogen nucleus. If after a symmetry operation all of the particles in an object are in the same conformation as before except for the exchange of identical particles, we say that the symmetry operator *belongs* to the object. Any object has a set of symmetry operators that belong to it. An unsymmetrical object possesses only the identity operator, but any symmetrical object possesses at least one additional symmetry operator. When we list the symmetry operators belonging to an object, we place the rotation axis of highest order (largest value of n) on the z axis and the center of mass of the object at the origin.

A uniform spherical object is the most highly symmetrical object. If the center of the sphere is at the origin, every mirror plane, every improper rotation axis, every proper rotation axis, and the inversion center at the origin are symmetry operators belonging to the sphere.

Example 13.12. List the symmetry operators belonging to a right circular cylinder.

Since all rotations belong to the cylinder, including an infinitesimal rotation, the z axis is a C_∞ axis. The symmetry operators are $\widehat{i},\widehat{C}_{\infty(z)},\widehat{S}_{\infty(z)},\hat{\sigma}_h,\infty\hat{\sigma}_v$ (infinitely many reflection operators with vertical symmetry elements), $\infty\widehat{C}_2$, (infinitely many $\widehat{C}_2$ operators with horizontal symmetry axes.

Exercise 13.12. List the symmetry elements of a uniform cube centered at the origin with its faces perpendicular to the coordinate axes.

Example 13.13. List the symmetry elements of the benzene molecule in its equilibrium conformation.

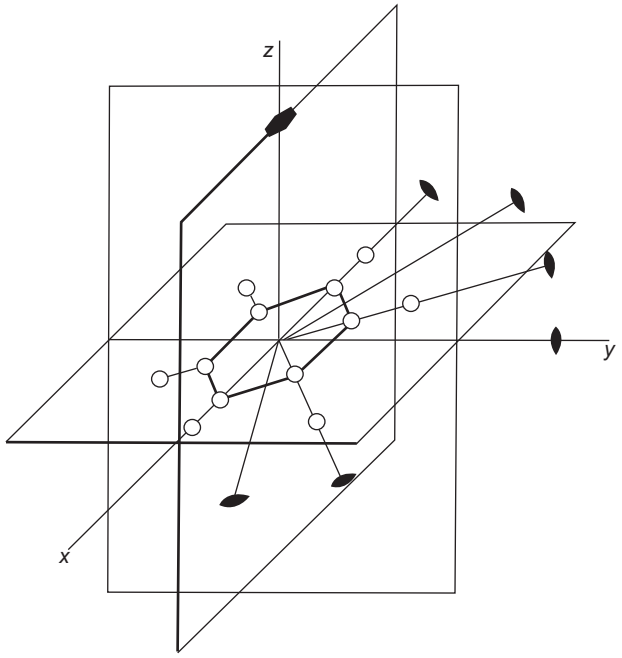

FIGURE 13.3 The benzene molecule with symmetry elements shown.

In its equilibrium conformation, the molecule is hexagonal, as depicted in Figure 13.3. The symmetry elements are:

A C_6 axis and an S_6 axis on the z axis;

The inversion center at the origin;

The σ_h mirror plane;

Six vertical mirror planes, three through carbon nuclei and three that lie halfway between adjacent carbon nuclei;

Six C_2 axes located where the mirror planes intersect the x–y plane. These are also S_2 axes;

Some of the symmetry elements are shown in Figure 13.3. The conventional symbols used to identify rotation axes are included: a hexagon labels a sixfold axis, a square labels a fourfold axis, a triangle labels a threefold axis, and a football-shaped object labels a twofold axis.

Exercise 13.13. List the symmetry elements for

(a) H_2O (bent).
(b) CO_2 (linear).

13.3 THE OPERATION OF SYMMETRY OPERATORS ON FUNCTIONS

Symmetry operators can operate on functions as well as on points, which places them on an equal footing with multiplication and differentiation operators. If $\widehat{O}$ is some symmetry operator such that

$$\widehat{O}(x_1,y_1,z_1) = (x_2,y_2,z_2). \tag{13.31}$$

and if ψ is some function of x, y, and z, we define

$$\widehat{O}\psi = \varphi, \tag{13.32}$$

where φ is a new function that has the same value at (x_2, y_2, z_2) that the original function ψ has at (x_1, y_1, z_1):

$$\boxed{\varphi(x_2, y_2, z_2) = \psi(x_1, y_1, z_1)}. \tag{13.33}$$

Example 13.14. The unnormalized $2px$ wave function for the electron in a hydrogen atom is

$$\psi_{2px} = x \exp\left[\frac{-(x^2 + y^2 + z^2)^{1/2}}{2a_0}\right],$$

where a_0 is the *Bohr radius*, equal to $0.529277349 \times 10^{-10}$ m. Find $\widehat{C}_{4(z)}\psi_{2px}$.

The effect of this operator on a point is given by

$$\widehat{C}_{4(z)}(x_1, y_1, z_1) = (x_2, y_2, z_2) = (-y_1, x_1, z_1).$$

The new function is thus

$$\begin{aligned}\phi(x_2, y_2, z_2) &= \psi_{2px}(x_1, y_1, z_1) \\ &= y_2 \exp\left[\frac{-(y_2^2 + x_2^2 + z_2^2)^{1/2}}{2a_0}\right].\end{aligned}$$

This is the same as the ψ_{2py} wave function

$$\widehat{C}_{4(z)}\psi_{2px} = \psi_{2py}.$$

The original function corresponds to a positive region in front of the x–z plane and a negative region behind the x–y plane. The symmetry operator has moved these regions in the same way that it moves a point.

Symmetry operators can have *eigenfunctions*. If a symmetry operator leaves a function unchanged, its eigenvalue is equal to unity. The only other possible eigenvalue for a symmetry operator is -1, which means that the operator changes the sign of the function's value at all points.

Exercise 13.14. Find $\widehat{i}\psi_{2px}$ where $\widehat{i}$ is the inversion operator. Show that ψ_{2px} is an eigenfunction of the inversion operator, and find its eigenvalue.

The most important quantum-mechanical operator is the *Hamiltonian operator*, which corresponds to the energy. The importance of symmetry operators in the study of electronic wave functions arises from the fact that two commuting operators can have a set of common eigenfunctions (eigenfunctions of both operators). An eigenfunction of the Hamiltonian operator can also be an eigenfunction of symmetry operators that commute with the Hamiltonian.

In the *Born-Oppenheimer approximation*, the electronic Hamiltonian operator operates on the coordinates of the electrons, but treats the nuclear coordinates as constants. The electronic Hamiltonian operator for a set of n electrons is

$$\widehat{H} = -\frac{\hbar}{2m_e}\sum_{n=1}^{n}\nabla_i^2 + \mathcal{V}, \tag{13.34}$$

where $\hbar$ is Planck's constant divided by 2π, where m_e is the electron mass, where ∇_i^2 is the Laplacian operator for electron number i, and where $\mathcal{V}$ is the potential energy as a function of the positions of the nuclei and electrons. If a symmetry operator leaves the potential energy unchanged when applied to the electrons' positions but not the nuclear positions, it will commute with the electronic Hamiltonian operator, and the eigenfunctions of the Hamiltonian operator can be eigenfunctions of that symmetry operator. A symmetry operator leaves the potential energy unchanged if it moves each electron so that it is the same distance from each nucleus or the same distance from another nucleus of the same charge as it was prior to the motion. Alternatively, you can apply the symmetry operator to the nuclei and not to the electrons to determine if the symmetry operator commutes with the Born-Oppenheimer Hamiltonian. If a symmetry operator either leaves every nucleus in the same position or places it in the original position of a nucleus of the same kind, it belongs to the nuclear framework and will commute with the electronic Hamiltonian when applied to the electrons but not to the nuclei.

Exercise 13.15. The potential energy of two electric charges Q_1 and Q_2 in a vacuum is

$$\mathcal{V} = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r_{12}},$$

where r_{12} is the distance between the charges and ε_0 is a constant called the permittivity of a vacuum, equal to $8.854187817 \times 10^{-12}$ F m^{-1} = $8.854187817 \times 10^{-12}$ C^2 N^{-1} m^{-2}. The potential energy of a hydrogen molecules is given by

$$\begin{aligned}\mathcal{V} = &\frac{e^2}{4\pi\varepsilon_0 r_{AB}} - \frac{e^2}{4\pi\varepsilon_0 r_{1A}} - \frac{e^2}{4\pi\varepsilon_0 r_{1B}} - \frac{e^2}{4\pi\varepsilon_0 r_{2A}} \\ &- \frac{e^2}{4\pi\varepsilon_0 r_{2B}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}},\end{aligned}$$

where A and B represent the nuclei and 1 and 2 represent the electrons, and where the two indexes indicate the two particles whose interparticle distance is denoted. If a hydrogen molecule is placed so that the origin is midway between the two nuclei and the nuclei are on the z axis show

that the inversion operator $\hat{i}$ and the reflection operator $\hat{\sigma}_h$ do not change the potential energy if applied to the electrons but not to the nuclei.

Full exploitation of the symmetry properties of electronic wave functions requires the use of group theory, which we briefly introduce in a later section of this chapter. However, we state two simple facts:

1. If a molecule has a permanent electric dipole moment, the dipole vector must lie along a proper rotation axis and in a plane of symmetry that belong to the molecule.
2. A molecule with an improper rotation axis cannot be optically active.

13.4 MATRIX ALGEBRA

We will find that matrices are useful in representing symmetry operations and will now present an elementary introduction to matrices. A *matrix* is a list of quantities arranged in rows and columns. If the matrix **A** has m rows and n columns, it is called an m by n matrix:

$$\mathbf{A} = \begin{bmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ a_{m1} & a_{m2} & a_{m3} & \cdots & a_{mn} \end{bmatrix}. \tag{13.35}$$

The quantities in the two-dimensional list are called *matrix elements*. Each matrix element has two subscripts, one for the row and one for the column. The brackets written on the left and right are part of the notation. If a matrix has the same number of rows as columns ($m = n$), it is a *square matrix*. A vector in ordinary space can be represented as a list of three Cartesian components, which is a matrix with one row and three columns. We call this a *row vector*. A vector can also be represented by a *column vector* with three rows and one column. We can also define row vectors and column vectors with more than three elements when they apply to something other than ordinary space. Just as there are types of algebra for scalars, vectors, and operators, there is a well-defined matrix algebra.

13.4.1 The Equality of Two Matrices

Two matrices are equal to each other if and only if they have the same number of rows and the same number of columns and if every element of one matrix is equal to the corresponding element of the other matrix.

13.4.2 The Sum of Two Matrices

The *sum of two matrices* is defined by

$$\mathbf{C} = \mathbf{A} + \mathbf{B} \quad \text{if and only if } c_{ij} = a_{ij} + b_{ij} \text{ for every } i \text{ and } j. \tag{13.36}$$

Two matrices can be added only if they have the same number of rows and the same number of columns.

13.4.3 The Product of a Scalar and a Matrix

The *product of a scalar c and a matrix* **A** is defined by

$$\mathbf{B} = c\mathbf{A} \quad \text{if and only if } b_{ij} = ca_{ij} \text{ for every } i \text{ and } j. \tag{13.37}$$

13.4.4 The Product of Two Matrices

The product of two matrices is analogous to the scalar produce of two vectors. If we rename the components of two vectors F_1, F_2, F_3, G_1, G_2, and G_3 instead of Fx, F_y, F_z, G_x, G_y, and G_z, we can write the scalar product of two vectors in Eq. (4.19) in the form

$$\mathbf{F} \cdot \mathbf{G} = F_1G_1 + F_2G_2 + F_3G_3 = \sum_{k=1}^{3} F_kG_k. \tag{13.38}$$

Matrix multiplication is defined for matrices that are not square and with any number of rows or columns. The number of columns in the left factor must equal the number of rows in the right factor. If **C** is the matrix product **AB**, we define the elements of **C** by the equation

$$c_{ij} = \sum_{k=1}^{n} a_{ik}b_{kj}. \tag{13.39}$$

In this equation, n is the number of columns in **A** and the number of rows in **B**. The matrix **C** will have as many rows as **A** and as many columns as **B**. Each element in **C** is obtained in the same way as taking a scalar product of a row from **A** and a column from **B**. In taking the matrix product, one moves along a row of the first matrix as one moves down a column of the second matrix as one forms the products of the matrix elements and adds them up. The result goes in the same row as the row in the first matrix and in the same column as the column in the second matrix.

If **A** is a 2 by 3 matrix and **B** is a 3 by 3 matrix, we can write their matrix product as

$$\begin{aligned} \mathbf{AB} &= \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \end{bmatrix} \begin{bmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{bmatrix} \\ &= \begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \end{bmatrix} = \mathbf{C}, \end{aligned} \tag{13.40}$$

where each element in the product matrix **C** is obtained as in Eq. (13.39). We can write the scalar product in Eq. (13.38) as a matrix product:

$$F \cdot G = [F_1 F_2 F_3] \begin{bmatrix} G_1 \\ G_2 \\ G_3 \end{bmatrix}.$$

This product has one row and one column (it is a scalar). Since a vector is represented as a matrix with one row or one column, you can have a product of a matrix with a vector. The product will be a vector.

Example 13.15. Find the matrix product

$$\begin{bmatrix} 1 & 0 & 2 \\ 0 & -1 & 1 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 0 & 2 \\ 3 & 0 & 1 \\ 1 & 1 & -1 \end{bmatrix} = \begin{bmatrix} 2 & 2 & 0 \\ -2 & 1 & -2 \\ 1 & 1 & -1 \end{bmatrix}.$$

Exercise 13.16. Find the product

$$\begin{bmatrix} 1 & 0 & 2 \\ 0 & -1 & 1 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ 3 \\ 1 \end{bmatrix}.$$

Vectors in ordinary space have three components. However, row and column vectors can have a number of elements other than three, just as a matrix can have a number of rows and columns other than three if they represent something other than a vector in three-dimensional space. Matrix multiplication with fairly large matrices can involve a lot of computation. Computer programs can be written to carry out the process, and such programs are built into Mathematica and into computer languages such as BASIC so that a matrix multiplication can be carried out with a single statement.

Two square matrices can be multiplied together in either order. However, the multiplication is not always *commutative*. It is possible that if **A** and **B** are square matrices

$$\boxed{\mathbf{AB} \neq \mathbf{BA} \text{ (in some cases)}}. \tag{13.41}$$

Exercise 13.17. Find the two matrix products

$$\begin{bmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \\ 1 & -1 & 2 \end{bmatrix} \begin{bmatrix} 1 & 3 & 2 \\ 2 & 2 & -1 \\ -2 & 1 & -1 \end{bmatrix}$$
$$\begin{bmatrix} 1 & 3 & 2 \\ 2 & 2 & -1 \\ -2 & -1 & -1 \end{bmatrix} \begin{bmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \\ 1 & -1 & 2 \end{bmatrix}.$$

The left factor in one product is equal to the right factor in the other product and vice versa. Are the two products equal to each other?

Matrix multiplication is *associative*,

$$\boxed{\mathbf{A}(\mathbf{BC}) = (\mathbf{AB})\mathbf{C}}. \tag{13.42}$$

Matrix multiplication and addition are *distributive*,

$$\boxed{\mathbf{A}(\mathbf{B} + \mathbf{C}) = \mathbf{AB} + \mathbf{AC}}. \tag{13.43}$$

Exercise 13.18. Show that the properties of Eqs. (13.42) and (13.43) are obeyed by the particular matrices

$$\mathbf{A} = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix}, \quad \mathbf{B} = \begin{bmatrix} 0 & 2 & 2 \\ -3 & 1 & 2 \\ 1 & -2 & -3 \end{bmatrix}, \quad \mathbf{C} = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 3 & -2 \\ 2 & 7 & -7 \end{bmatrix}.$$

13.4.5 The Identity Matrix

We now define the identity matrix **E** such that

$$\boxed{\mathbf{EA} = \mathbf{AE} = \mathbf{A}}.$$

The fact that we require **E** to be the identity matrix when multiplied on either side of **A** requires both **A** and **E** to be square matrices. With square matrices we will get a complete similarity between operator algebra and matrix algebra. An identity matrix can have any number of rows and columns. It has the form

$$\mathbf{E} = \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 \\ 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 1 \end{bmatrix}. \tag{13.44}$$

The *diagonal elements* of any square matrix are those with both indices equal. The diagonal elements of **E** are all equal to 1and the other elements (*off-diagonal elements*) vanish. This can be represented by the equation

$$E_{ij} = \delta_{ij} = \begin{cases} 1 \text{ if } i = j, \\ 0 \text{ if } i \neq j, \end{cases}$$

where δ_{ij} is called the *Kronecker delta*.

Exercise 13.19. Show by explicit matrix multiplication that

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{31} & a_{41} \\ a_{31} & a_{31} & a_{31} & a_{41} \\ a_{41} & a_{41} & a_{31} & a_{41} \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{21} & a_{31} & a_{41} \\ a_{31} & a_{31} & a_{31} & a_{41} \\ a_{41} & a_{41} & a_{31} & a_{41} \end{bmatrix}.$$

13.4.6 The Inverse of a Matrix

We denote the inverse of the matrix $\mathbf{A}$ by $\mathbf{A}^{-1}$, and define it such that

$$\boxed{\mathbf{A}\mathbf{A}^{-1} = \mathbf{E}}. \tag{13.45}$$

Only square matrices have inverses, and some of them do not, as we discuss later. The multiplication of a matrix by its inverse is commutative, so that $\mathbf{A}$ is also the inverse of $\mathbf{A}^{-1}$.

$$\boxed{\mathbf{A}\mathbf{A}^{-1} = \mathbf{A}^{-1}\mathbf{A} = \mathbf{E}}. \tag{13.46}$$

In terms of matrix elements

$$\sum_{k=1}^{n} a_{ik}(A^{-1})_{kj} = \delta_{ij}, \tag{13.47}$$

where we write $(\mathbf{A}^{-1})_{kj}$ for the kj element of $\mathbf{A}^{-1}$. This equation represents a set of simultaneous linear algebraic equations, one for each value of i and each value of j, so that there are just enough equations to determine the elements of $\mathbf{A}^{-1}$.

One method for finding $\mathbf{A}^{-1}$ is called *Gauss–Jordan elimination*, which is a method of solving simultaneous linear algebraic equations. It consists of a set of operations to be applied to Eq. (13.45). Each operation is applied to the matrix $\mathbf{A}$ and to the matrix $\mathbf{E}$ on the right-hand side (13.45), but not to the unknown matrix $\mathbf{A}^{-1}$. This is analogous to the fact that if you have an equation $ax = c$, you could multiply a and c by some factor, but not multiply both a and x by the factor. We apply *row operations*. For example, we might multiply every element in a given row of $\mathbf{A}$ by some constant and multiply every element in the same row of $\mathbf{E}$ by the same constant. Another row operation is to subtract one row of $\mathbf{A}$ from another row of $\mathbf{A}$, element by element, while doing the same thing to $\mathbf{E}$. This amounts to subtracting the left-hand sides of pairs of equations and subtracting at the same time the right-hand sides of the equations. We can also replace one of the rows by the difference of two rows.

The goal of the operations is to transform Eq. (13.45) into

$$\mathbf{E}\left(\mathbf{A}^{-1}\right) = \mathbf{D}, \tag{13.48}$$

so that $\mathbf{A}^{-1}$ will be the same matrix as the newly constructed matrix $\mathbf{D}$. Successive application of two row operations can transform the left factor of the matrix product into the identity matrix while transforming the right-hand side of the equation into the inverse matrix. In order to carry out the procedure conveniently, we write the matrix $\mathbf{A}$ and the matrix $\mathbf{E}$ side by side and carry out operations on each element of the same row in the augmented matrix.

Example 13.16. Find the inverse of the matrix

$$\mathbf{A} = \begin{bmatrix} 2 & 1 & 0 \\ 1 & 2 & 1 \\ 0 & 1 & 2 \end{bmatrix}.$$

Our version of Eq. (13.45) is

$$\begin{bmatrix} 2 & 1 & 0 \\ 1 & 2 & 1 \\ 0 & 1 & 2 \end{bmatrix} \begin{bmatrix} (A^{-1})_{11} & (A^{-1})_{12} & (A^{-1})_{13} \\ (A^{-1})_{21} & (A^{-1})_{22} & (A^{-1})_{23} \\ (A^{-1})_{22} & (A^{-1})_{32} & (A^{-1})_{33} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

We write the two matrices on which we operate side by side as an augmented matrix and perform the same operations on the same row of both matrices. The matrix that is not operated on, A^{-1}, is not written. The augmented matrix is:

$$\begin{bmatrix} 2 & 1 & 0 & \cdots & 1 & 0 & 0 \\ 1 & 2 & 1 & \cdots & 0 & 1 & 0 \\ 0 & 1 & 2 & \cdots & 0 & 0 & 1 \end{bmatrix}.$$

We want to replace the off-diagonal matrix elements by zeros and the diagonal elements by ones. It is usual to clear out the columns from left to right. We first want to get a zero in the place of a_{21}. We multiply the first row by $\frac{1}{2}$, obtaining

$$\begin{bmatrix} 1 & \frac{1}{2} & 0 & \cdots & \frac{1}{2} & 0 & 0 \\ 1 & 2 & 1 & \cdots & 0 & 1 & 0 \\ 0 & 1 & 2 & \cdots & 0 & 0 & 1 \end{bmatrix}.$$

We subtract the first row from the second and replace the second row by this difference. The result is

$$\begin{bmatrix} 1 & \frac{1}{2} & 0 & \cdots & \frac{1}{2} & 0 & 0 \\ 0 & \frac{3}{2} & 1 & \cdots & -\frac{1}{2} & 1 & 0 \\ 0 & 1 & 2 & \cdots & 0 & 0 & 1 \end{bmatrix}.$$

We say that we have used the element a_{11} as the pivot element. The left column is now as we want it to be. We now use the a_{22} element as the pivot element to clear the second column. We multiply the second row by $\frac{1}{3}$ and replace the first row by the difference of the first row and the second to obtain

$$\begin{bmatrix} 1 & 0 & -\frac{1}{3} & \cdots & \frac{2}{3} & -\frac{1}{3} & 0 \\ 0 & \frac{1}{2} & \frac{1}{3} & \cdots & -\frac{1}{6} & \frac{1}{3} & 0 \\ 0 & 1 & 2 & \cdots & 0 & 0 & 1 \end{bmatrix}.$$

We now multiply the second row by 2, subtract this row from the third row, and replace the third row by the difference. The result is

$$\begin{bmatrix} 1 & 0 & -\frac{1}{3} & \cdots & \frac{2}{3} & -\frac{1}{3} & 0 \\ 0 & 1 & \frac{2}{3} & \cdots & -\frac{1}{3} & \frac{2}{3} & 0 \\ 0 & 0 & \frac{4}{3} & \cdots & \frac{1}{3} & -\frac{2}{3} & 1 \end{bmatrix}.$$

We now multiply the third row by $\frac{1}{2}$ in order to use the a_{33} element as the pivot element. We subtract the third row from the second and replace the second row by the difference, obtaining

$$\begin{bmatrix} 1 & 0 & -\frac{1}{3} & \cdots & \frac{2}{3} & -\frac{1}{3} & 0 \\ 0 & 1 & 0 & \cdots & -\frac{1}{2} & 1 & -\frac{1}{2} \\ 0 & 0 & \frac{2}{3} & \cdots & \frac{1}{6} & -\frac{1}{3} & \frac{1}{2} \end{bmatrix}.$$

We now multiply the third row by $\frac{1}{2}$, add it to the first row, and replace the first row by the sum. The result is

$$\begin{bmatrix} 1 & 0 & 0 & \cdots & \frac{3}{4} & -\frac{1}{2} & \frac{1}{4} \\ 0 & 1 & 0 & \cdots & -\frac{1}{2} & 1 & -\frac{1}{2} \\ 0 & 0 & \frac{1}{3} & \cdots & \frac{1}{12} & -\frac{1}{6} & \frac{1}{4} \end{bmatrix}.$$

We multiply the third row by 3 to obtain

$$\begin{bmatrix} 1 & 0 & 0 & \cdots & \frac{3}{4} & -\frac{1}{2} & \frac{1}{4} \\ 0 & 1 & 0 & \cdots & -\frac{1}{2} & 1 & -\frac{1}{2} \\ 0 & 0 & 1 & \cdots & \frac{1}{4} & -\frac{1}{2} & \frac{3}{4} \end{bmatrix}.$$

The right half of the augmented matrix is A^{-1}:

$$\mathbf{A}^{-1} = \begin{bmatrix} \frac{3}{4} & -\frac{1}{2} & \frac{1}{4} \\ -\frac{1}{2} & 1 & -\frac{1}{2} \\ \frac{1}{4} & -\frac{1}{2} & \frac{3}{4} \end{bmatrix}.$$

Exercise 13.20. Show that $\mathbf{A}\mathbf{A}^{-1} = \mathbf{E}$ and that $\mathbf{A}^{-1}\mathbf{A} = \mathbf{E}$ for the matrices of the preceding example.

Mathematica and other software packages can find the inverse of a square matrix with a single command.

Exercise 13.21. Use Mathematica or another software package to verify the inverse found in the preceding example.

Exercise 13.22. Find the inverse of the matrix

$$\mathbf{A} = \begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix}.$$

Not all square matrices have inverses. Associated with each square matrix is a determinant, which we define in the next section. If the determinant of a square matrix vanishes, the matrix is said to be *singular*. A singular matrix has no inverse.

13.4.7 Matrix Terminology

We conclude this section with the definition of several terms that apply to square matrices. The *trace* of a matrix is the sum of the diagonal elements of the matrix:

$$Tr(\mathbf{A}) = \sum_{i=1}^{n} a_{ii} \text{ (definition)} \tag{13.49}$$

The trace is sometimes called the *spur*, from the German word *Spur*, which means track or trace. For example, the trace of the n by n identity matrix is equal to n.

A matrix in which all the elements below the diagonal elements vanish is called an *upper triangular matrix*. A matrix in which all the elements above the diagonal elements vanish is called a *lower triangular matrix*, and a matrix in which all the elements except the diagonal elements vanish is called a *diagonal matrix*. The matrix in which all of the elements vanish is called the *null matrix* or the *zero matrix*. The *transpose* of a matrix is obtained by replacing the first column by the first row, the second column by the second row of the original matrix, and so on. The transpose of $\mathbf{A}$ is denoted by $\widetilde{\mathbf{A}}$ (pronounced "A tilde"),

$$(\widetilde{\mathbf{A}})_{ij} = \widetilde{a}_{ij} = a_{ji}. \tag{13.50}$$

If a matrix is equal to its transpose, it is a *symmetric matrix*.

The *hermitian conjugate* of a matrix is obtained by taking the complex conjugate of each element and then taking the transpose of the resulting matrix. The hermitian conjugate is denoted by $\mathbf{A}^{\dagger}$. If a matrix has only real elements, the hermitian conjugate is the same as the transpose. The hermitian conjugate is also called the *adjoint* (mostly by physicists) and the *associate* (mostly by mathematicians, who use the term "adjoint" for something else).

$$(\mathbf{A}^{\dagger})_{ij} = a^*_{ji}. \tag{13.51}$$

A matrix that is equal to its hermitian conjugate is said to be a *hermitian matrix*. An *orthogonal matrix* is one whose inverse is equal to its transpose. If $\mathbf{A}$ is orthogonal, then

$$\mathbf{A}^{-1} = \widetilde{\mathbf{A}} \quad \text{(orthogonal matrix)}. \tag{13.52}$$

A *unitary matrix* is one whose inverse is equal to its hermitian conjugate. If $\mathbf{A}$ is unitary, then

$$\mathbf{A}^{-1} = \mathbf{A}^{\dagger} = \widetilde{\mathbf{A}}^* \quad \text{(unitary matrix)}. \tag{13.53}$$

13.5 DETERMINANTS

Associated with every square matrix is a quantity called a *determinant*. The elements of the determinant are the same as those of the matrix, but there is a defined set of operations that are carried out on the elements to determine its value,

which is a scalar. The value of a 2 by 2 determinant is defined as the product of the diagonal elements minus the product of the off-diagonal elements:

$$\det(\mathbf{A}) = \det\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{12}a_{21}. \tag{13.54}$$

The determinant is denoted by straight vertical line segments on the left and right of the array of elements. Finding the value of a determinant is called *expanding the determinant* . If the elements of a determinant are constants, its value is a single constant.

Example 13.17. Find the value of the determinant

$$\begin{vmatrix} 3 & -17 \\ 1 & 5 \end{vmatrix}.$$

$$\begin{vmatrix} 3 & -17 \\ 1 & 5 \end{vmatrix} = (3)(5) - (-17)(1) = 15 + 17 = 32.$$

Finding the value of a determinant larger than 2 by 2 requires a number of operations. One way to proceed it is by *expanding by minors* as follows:

1. Pick a row or a column of the determinant. Any row or column will do, but one with zeros in it will minimize the work.
2. The determinant is equal to a sum of terms, one for each element in this row or column. Each term consists of an element of the chosen row or column times the *minor* of that element, with an assigned sign, either positive or negative. The minor of an element in a determinant is obtained by deleting the row and the column containing that element. It is a determinant with one less row and one less column than the original determinant.
3. Determine the sign assigned to a term as follows: Count the number of steps of one row or one column required to get from the upper left element to the element whose minor is desired. Diagonal steps are not allowed. If the number of steps is odd, the sign is negative. If the number of steps is even (including zero), the sign is positive.
4. Repeat the entire process with each determinant in the expansion until you have a sum of 2 by 2 determinants, which can be evaluated by Eq. (13.54).

The *cofactor* of an element in a determinant is the minor multiplied by the appropriate factor of 1 or -1, determined as in Step 3.

Example 13.18. Expand the 3 by 3 determinant of the matrix **A** by minors.

$$\begin{aligned}\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} &= a_{11}\begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12}\begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} \\ &\quad + a_{13}\begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix} \\ &= a_{11}a_{22}a_{33} - a_{11}a_{23}a_{32} - a_{12}a_{21}a_{33} \\ &\quad + a_{12}a_{23}a_{31} + a_{13}a_{21}a_{32} - a_{13}a_{22}a_{31}.\end{aligned}$$

Exercise 13.23. Expand the following determinant by minors:

$$\begin{vmatrix} 3 & 2 & 0 \\ 7 & -1 & 5 \\ 2 & 3 & 4 \end{vmatrix}.$$

Determinants have a number of important properties:

1. If every element in any one row or in any one column of a determinant is zero, the value of the determinant is zero.
2. If two rows or two columns of a determinant are identical, the determinant has value zero.
3. If two rows of a determinant are interchanged, the result will be a determinant whose value is the negative of the value of the original determinant. The same is true if two columns are interchanged.
4. If each element in one row or one column of a determinant is multiplied by the same quantity c, the value of the new determinant is c times the value of the original determinant. If every element of an n by n determinant is multiplied by c, the new determinant is c^n times the original determinant.
5. If any row is replaced, element by element, by that row plus a constant times another row, the value of the determinant is unchanged. The same is true for two columns. For example,

$$\begin{vmatrix} a_{11} + ca_{12} & a_{12} & a_{13} \\ a_{21} + ca_{22} & a_{22} & a_{13} \\ a_{31} + ca_{32} & a_{32} & a_{33} \end{vmatrix} = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}. \tag{13.55}$$

6. The determinant of a triangular matrix (a *triangular determinant*) is equal to the product of the diagonal elements. For example,

$$\begin{vmatrix} a_{11} & 0 & 0 \\ a_{22} & a_{22} & 0 \\ a_{21} & a_{32} & a_{33} \end{vmatrix} = a_{11}a_{22}a_{33}. \tag{13.56}$$

This statement is true whether the determinant is an upper triangular determinant or a lower triangular determinant.

7. The determinant of a matrix is equal to the determinant of the transpose of that matrix.

$$\det(\widetilde{\mathbf{A}}) = \det(\mathbf{A}). \tag{13.57}$$

These properties can be verified using the expansion of a determinant by minors.

Exercise 13.24. (a) Find the value of the determinant

$$\begin{vmatrix} 3 & 4 & 5 \\ 2 & 1 & 6 \\ 3 & -5 & 10 \end{vmatrix}.$$

(b) Interchange the first and second columns and find the value of the resulting determinant.
(c) Replace the second column by the sum of the first and second columns and find the value of the resulting determinant.
(d) Replace the second column by the first, thus making two identical columns, and find the value of the resulting determinant.

There is an application of determinants in quantum chemistry that comes from Property 2 and Property 3. The electronic wave function of a system containing two or more electrons must change sign if the coordinates of two of the electrons are interchanged (the wave function must be *antisymmetric*) . For example, if $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of two electrons and $\boldsymbol{\Psi}$ is a multi-electron wave function, then the wave function must obey

$$\boldsymbol{\Psi}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4,\ldots,\mathbf{r_n}) = -\boldsymbol{\Psi}(\mathbf{r}_2,\mathbf{r}_1,\mathbf{r}_3,\mathbf{r}_4,\ldots,\mathbf{r_n}) \tag{13.58}$$

with similar equations for exchanging any other pair of electrons' coordinates. Many approximate multi-electron wave functions are constructed as a product of one-electron wave functions, or *orbitals*. If ψ_1, ψ_2, and so on, are orbitals such a wave function for n electrons is written as

$$\boldsymbol{\Psi} = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\psi_3(\mathbf{r}_3)\psi_4(\mathbf{r}_4)\cdots\psi_n(\mathbf{r_n}), \tag{13.59}$$

where $\mathbf{r}_1, \mathbf{r}_2, \ldots$ represent the coordinates of electron 1, electron 2 and so on. This wave function does not necessarily obey the antisymmetry condition of Eq. (13.58). A wave function that does obey this equation can be constructed as a *Slater determinant*. [4] The elements of this determinant are the orbital functions, so the determinant is equal to a function of the coordinates of all electrons. The Slater determinant is constructed by making a row for each orbital factor and assigning the coordinates of the n electrons as the independent variables in sequence across the row:

$$\boldsymbol{\Psi}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r_n}) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \psi_1(\mathbf{r}_3) & \cdots & \psi_{|}(\mathbf{r_n}) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \psi_2(\mathbf{r}_3) & \cdots & \psi_2(\mathbf{r_n}) \\ \psi_3(\mathbf{r}_1) & \psi_3(\mathbf{r}_2) & \psi_3(\mathbf{r}_3) & \cdots & \psi_3(\mathbf{r_n}) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_n(\mathbf{r}_1) & \psi_n(\mathbf{r}_2) & \psi_n(\mathbf{r}_3) & \cdots & \psi_n(\mathbf{r_n}) \end{vmatrix}. \tag{13.60}$$

The factor $1/\sqrt{n!}$ is a normalizing factor. The Slater determinant obeys the antisymmetry property, since interchanging $\mathbf{r}_1$ and $\mathbf{r}_2$, for example, is the same as interchanging two columns, which changes the sign of the determinant. If we attempt to write such a wave function with two electrons in the same orbital (two of the ψ factors identical), then two rows of the determinant are identical, and the entire determinant vanishes by Property 2. This is the *Pauli exclusion principle*, which states that no two electrons in the same atom or molecule can occupy the same orbital.[5] For n electrons, the expanded Slater determinant consists of $n!$ (n factorial) terms, where $n! = n(n-1)(n-2)(n-3)\cdots(3)(2)(1)$.

13.6 MATRIX ALGEBRA WITH MATHEMATICA

Matrix algebra can be tedious. Mathematica has all of the matrix operations built into it, so that you can form matrix products and carry out matrix inversion automatically. Mathematica treats matrices as lists of lists, with the elements of each row entered as a list. A list is entered inside curly brackets ("braces") with the elements separated by commas. A list of lists requires braces around the set of lists with braces and commas. For example, to enter the following 3 by 3 matrix

$$\mathbf{A} = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} \tag{13.61}$$

you would type in the following

```
Clear[a]
a = {{1, 2, 3}, {4, 5, 6},{7, 8, 9}}
```

and press the "Enter" key or a "Shift-Return." Mathematica will type the following:

```
In[1]: a = {{1, 2, 3}, {4, 5, 6},{7, 8, 9}}
```

[4] After John C. Slater, 1900–1976, a prominent American physicist and chemist.

[5] The Pauli exclusion principle is named for Wolfgang Pauli, 1900–1958, who received the 1945 Nobel Prize in physics for his contributions to quantum mechanics.

Note that the symbol that we chose for the matrix name is in lower case and requires no auxiliary labels. You should start the names of all Mathematica variables with lowercase letters to avoid possible confusion with Mathematica operators and functions. If you want to see the matrix **A** in standard form, type the statement MatrixForm[a] and press the "Enter" key or the "Shift-Return."

Mathematica treats vectors as a single list. It does not distinguish between row vectors and column vectors. If you want to enter a vector $v = (2, 4, 6)$, you enter the components inside curly brackets separated by commas as follows:

```
v = {2,4,6}
```

followed by pressing the "Enter" key in the numeric keypad or a "Shift-Return." A diagonal matrix is entered as a single list inside square brackets. To enter the diagonal matrix

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 4 \end{bmatrix} \tag{13.62}$$

use the statement

```
DiagonalMatrix[{1, 2, 4}]
```

When you press "Enter" or "Shift-Return," you get the output.

```
Out[1]={{1,0,0,},{0,2,0,},{0,0,4}}
```

After two matrices A and B have been entered, a matrix multiplication is carried out by the statement.

```
a.b
```

where you type a period between the symbols for the matrices. The product of a row vector with a matrix is accomplished with the statement.

```
v.a
```

and a product of a matrix and a column vector is accomplished with the statement.

```
a.v
```

The inverse of a matrix is obtained with the statement.

```
Inverse[a]
```

If the matrix is singular and does not have an inverse, Mathematica will tell you so. To obtain the determinant of a square matrix **A**, use the statement.

```
Det[a]
```

Remember the capitalization. Mathematica does not allow alternate choices to its statements.

Exercise 13.25. Obtain the inverse of the following matrix by hand. Then use Mathematica to verify your answer.

$$\begin{bmatrix} 1 & 3 & 0 \\ 3 & 0 & 4 \\ 1 & 2 & 0 \end{bmatrix}.$$

Mathematica is a large and powerful program, and you can refer to the book by Wolfram listed at the end of this book to learn more about its use.

13.7 AN ELEMENTARY INTRODUCTION TO GROUP THEORY

A mathematical *group* is a collection of members with a single method for combining two members of the group. We call this method multiplication in order to exploit the similarities of this operation with matrix and operator multiplication. The following requirements must be met for a collection of members to be a group:

1. If **A** and **B** are members of the group, and **F** is the product **AB**, then **F** must be a member of the group.
2. The group must contain the identity, **E**, such that for every member **A**

$$\mathbf{AE} = \mathbf{EA} = \mathbf{A}. \tag{13.63}$$

3. The inverse of every member of the group must be a member of the group.

$$\mathbf{A}^{-1}\mathbf{A} = \mathbf{A}\mathbf{A}^{-1} = \mathbf{E}. \tag{13.64}$$

4. The associative law must hold:

$$\mathbf{A}(\mathbf{BC}) = (\mathbf{AB})\mathbf{C}. \tag{13.65}$$

It is not necessary that the members of the group commute with each other. That is, it is possible that

$$\mathbf{AB} \neq \mathbf{BA} \text{ (possible but not required).}$$

If all the members of the group commute with each other, the group is called *abelian*.[6]

The set of symmetry operators belonging to a symmetrical object forms a group if we define operator multiplication to be the method of combining two members of the group. We illustrate this fact for the ammonia

[6] After Niels Henrik Abel, 1802–1829, a great Norwegian mathematician, who was the first to show that a general fifth-degree algebraic equation cannot be solved by a radical expression.

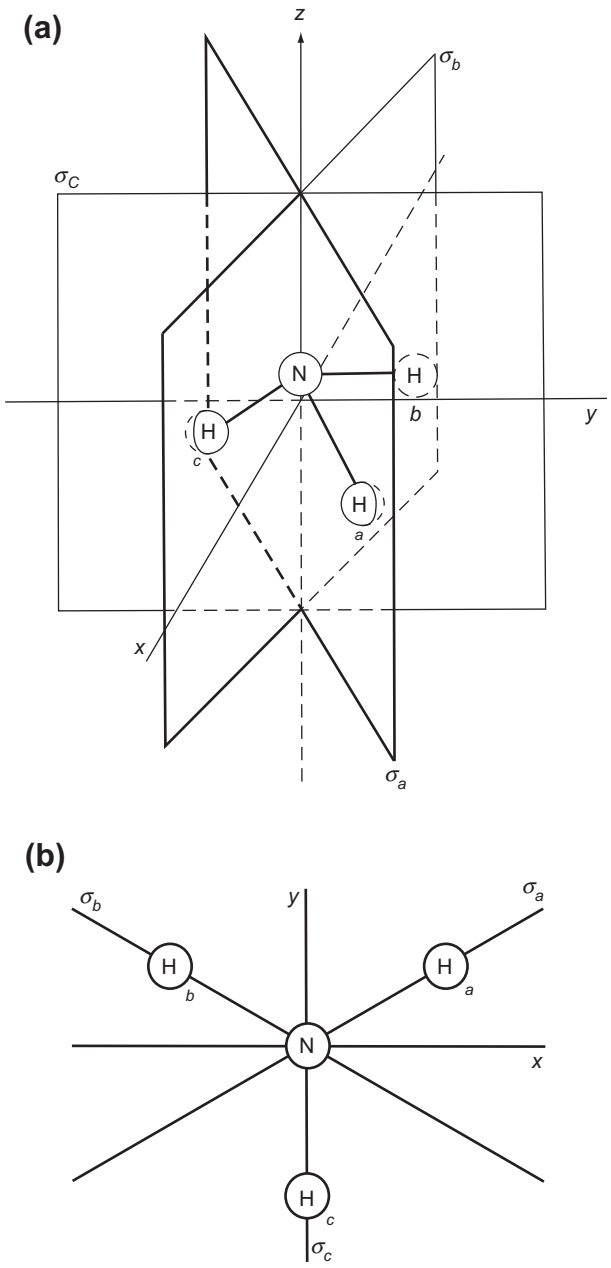

FIGURE 13.4 (a) The NH_3 molecule in its coordinate axes, with symmetry elements shown (after Levine). (b) The NH_3 molecule viewed from the positive z axis (after Levine).

molecule , NH_3. In its equilibrium conformation, the nuclei of molecule form a triangular pyramid.[7] Figure 13.4a shows the nuclei as viewed from the first octant of the coordinate system, and Figure 13.4b shows the framework as viewed from the positive end of the z axis. The molecule is placed in the coordinate system in the conventional way, with the center of mass at the origin and the threefold rotation axis along the z axis.

The symmetry elements of the molecule are shown in the figure. The symmetry operators that belong to the nuclear framework are $\widehat{E}, \widehat{C}_3, \widehat{C}_3^2$ and the three reflection operators corresponding to vertical mirror planes passing through each of the three hydrogen nuclei, which we call $\hat{\sigma}_a, \hat{\sigma}_b$, and $\hat{\sigma}_c$. The square of the $\widehat{C}_3$ operator is included because we must include the inverse of all operators in the group and $\widehat{C}_3^2$ is the inverse of $\widehat{C}_3$. A rotation of 120° in the clockwise direction is the inverse of $\widehat{C}_3$ and a rotation of 240° in the counterclockwise direction gives the same result as this.)

We now show that the four conditions to have a group are met:

Condition 1. The product of any two members of the group must be a member of the group. We show this by constructing a multiplication table, as shown in Table 13.1.

The operators listed in the first row of the table are used as the right factor in a product, and the operators listed in the first column of the table are used as the left factor. We must specify which factor comes first because the operators do not necessarily commute. The entries in the table are obtained as in the example:

Condition 2. *The group does contain the identity operator,* $\widehat{E}$.

Condition 3. The inverse of every operator is in the group. Each reflection operator is its own inverse, and the inverse of $\widehat{C}_3$ is $\widehat{C}_3^2$.

Condition 4. The multiplication operation is associative, because operator multiplication is always associative.

TABLE 13.1 Multiplication Table for the Symmetry Operators of the NH_3 Molecule

	$\widehat{E}$	$\widehat{C}_3$	$\widehat{C}_3^2$	$\hat{\sigma}_a$	$\hat{\sigma}_b$	$\hat{\sigma}_c$
$\widehat{E}$	$\widehat{E}$	$\widehat{C}_3$	$\widehat{C}_3^2$	$\hat{\sigma}_a$	$\hat{\sigma}_b$	$\hat{\sigma}_c$
$\widehat{C}_3$	$\widehat{C}_3$	$\widehat{C}_3^2$	$\widehat{E}$	$\hat{\sigma}_c$	$\hat{\sigma}_a$	$\hat{\sigma}_b$
$\widehat{C}_3^2$	$\widehat{C}_3^2$	$\widehat{E}$	$\widehat{C}_3$	$\hat{\sigma}_b$	$\hat{\sigma}_c$	$\hat{\sigma}_a$
$\hat{\sigma}_a$	$\hat{\sigma}_a$	$\hat{\sigma}_b$	$\hat{\sigma}_c$	$\widehat{E}$	$\widehat{C}_3$	$\widehat{C}_3^2$
$\hat{\sigma}_b$	$\hat{\sigma}_b$	$\hat{\sigma}_c$	$\hat{\sigma}_a$	$\widehat{C}_3^2$	$\widehat{E}$	$\widehat{C}_3$
$\hat{\sigma}_c$	$\hat{\sigma}_c$	$\hat{\sigma}_a$	$\hat{\sigma}_b$	$\widehat{C}_3$	$\widehat{C}_3^2$	$\widehat{E}$

[7] This discussion is adapted from Ira N. Levine, *Molecular Spectroscopy*, pp. 390ff, Wiley, New York, 1975.

Some pairs of operators in this group commute, whereas others do not. For example, $\widehat{C}_3$ and $\hat{\sigma}_c$ do not commute: $\widehat{C}_3\hat{\sigma}_c = \hat{\sigma}_b$, whereas $\hat{\sigma}_c\widehat{C}_3 = \hat{\sigma}_a$.

Example 13.19. Find the product $\hat{\sigma}_c\widehat{C}_3$.

Both of these operators leave the nitrogen nucleus in its original location. The $\widehat{C}_3$ operator moves the hydrogen nucleus originally at the σ_a plane to the σ_b plane, the nucleus originally at the σ_b plane to the σ_c plane, and the nucleus originally at the σ_c plane to the σ_a plane. The $\hat{\sigma}_c$ operator reflects in the σ_c plane, so that it exchanges the nuclei at the σ_a and σ_b planes. It thus returns the nucleus originally at the σ_{ct} plane to its original position and moves the nucleus originally at the σ_c plane to the σ_b plane. This is the same as the effect that the $\hat{\sigma}_a$ operator would have, so that

$$\hat{\sigma}_c\widehat{C}_3 = \hat{\sigma}_a.$$

A group that consists of point symmetry operators is called a *point group*. Each point group is assigned a symbol, called a *Schoenflies symbol*. The point group of the NH_3 molecule is called the C_{3v} group. This symbol is chosen because the principal rotation axis is a C_3 axis, and because there are vertical mirror planes. You can communicate what the symmetry properties of the NH_3 molecule are by saying that it has C_{3v} symmetry. Flow charts have been constructed for the routine assignment of Schoenflies symbols.[8]

The H_2O molecule belongs to the C_{2v} point group, which contains the operators $\widehat{E}, \widehat{C}_2$, and two reflection operators, one whose mirror plane is the plane of the three nuclei and one whose mirror plane bisects the angle between the bonds and is perpendicular to the first.

Exercise 13.26. Obtain the multiplication table for the C_{2v} point group and show that it satisfies the conditions to be a group.

13.8 SYMMETRY OPERATORS AND MATRIX REPRESENTATIONS

Operator algebra and matrix algebra are similar to each other. A set of matrices can be a *representation* of a group of symmetry operators if there is a matrix corresponding to each of the symmetry operators and if the matrices obey the same multiplication table as the symmetry operators. We now show how one such representation can be constructed. Equation (13.21) represents the action of a general symmetry operator, $\widehat{A}$, on the location of a point. We rewrite this equation in the form:

$$\widehat{A}(x,y,z) = (x',y',z'). \tag{13.66}$$

[8] See, for example, Peter Atkins, Julio de Paula, and Ronald Friedman, *Quanta, Matter, and Change*, Freeman, New York, 2009, p. 199.

If we represent the position vectors by 3 by 1 matrices (column vectors), Eq. (13.66) can be written as a matrix equation:

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}. \tag{13.67}$$

Equation (13.67) is the same as three ordinary equations:

$$a_{11}x + a_{12}y + a_{13}z = x', \tag{13.68}$$
$$a_{21}x + a_{22}y + a_{23}z = y', \tag{13.69}$$
$$a_{31}x + a_{32}y + a_{33}z = z'. \tag{13.70}$$

We can obtain the elements of the matrix that corresponds to a given symmetry operator by comparing these equations with the equations obtained in Section 13.2. For example, in the case of the identity operator, $x = x', y = y'$, and $z = z'$, so that the matrix for the identity symmetry operator is the 3 by 3 identity matrix.

$$\widehat{E} \leftrightarrow \mathbf{E} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{13.71}$$

The double-headed arrow means that the symmetry operator $\widehat{E}$ and the matrix $\mathbf{E}$ are equivalent. That is, the matrix product in Eq. (13.67) and the operator expression in Eq. (13.66) give the same result. We say that there is a *one-to-one correspondence* between this operator and this matrix.

Example 13.20. Find the matrix that represents $\widehat{C}_{n(z)}$.

Let $\alpha = 2\pi/n$ radians, the angle through which the operator rotates a particle,

$$x' = \cos(\alpha)x - \sin(\alpha)y,$$
$$y' = \sin(\alpha)x + \cos(\alpha)y,$$
$$z' = z.$$

$$\widehat{C}_{n(z)} \leftrightarrow \begin{bmatrix} \cos(\alpha) & -\sin(\alpha) & 0 \\ \sin(\alpha) & \cos(\alpha) & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Exercise 13.27. **(a)** Find the matrix equivalent to $\widehat{C}_{2(z)}$.

(b) Find the matrix equivalent to $\widehat{S}_{3(z)}$.

(c) Find the matrix equivalent to $\hat{\sigma}_h$.

When we find the 3 by 3 matrices that perform the same transformations as the operators in the C_{3v} group, we obtain

the following representation of the C_{3v} group:

$$\widehat{E} \leftrightarrow \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{E},$$

$$\widehat{C}_3 \leftrightarrow \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{A},$$

$$\widehat{C}_3^2 \leftrightarrow \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{B},$$

$$\hat{\sigma}_a \leftrightarrow \begin{bmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{C},$$

$$\hat{\sigma}_b \leftrightarrow \begin{bmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{D},$$

$$\hat{\sigma}_c \leftrightarrow \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{F}, \qquad (13.72)$$

where we have given each matrix an arbitrarily chosen letter symbol. Some pairs of operators in this group commute, whereas others do not. For example, $\widehat{C}_3$ and $\hat{\sigma}_c$ do not commute: $\widehat{C}_3\hat{\sigma}_c = \hat{\sigma}_b$, whereas $\hat{\sigma}_c\widehat{C}_3 = \hat{\sigma}_a$. These matrices obey the same multiplication table as the symmetry operators.

Exercise 13.28. By transcribing Table 13.1 with appropriate changes in symbols, generate the multiplication table for the matrices in Eq. (13.72).

Example 13.21. By matrix multiplication, show that $\mathbf{AB} = \mathbf{E}$.

$$\begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Exercise 13.29. Verify several of the entries in the multiplication table by matrix multiplication of the matrices in Eq. (13.72).

Each of the matrices in Eq. (13.72) is equivalent to one of the symmetry operators in the C_{3v} group, but there can be other representations of the C_{3v} group. Any set of matrices that obeys the same multiplication table as a given group is a *representation* of that group. Our set of matrices forms another group of the same *order* (same number of members) as the C_{3v} point group. The fact that it obeys the same multiplication table is expressed by saying that it is *isomorphic* with the group of symmetry operators. A group of matrices that is isomorphic with a group of symmetry operators is called a *faithful representation* of the group. Our group of matrices consists of 3 by 3 matrices and is said to be of *dimension* 3.

The representation of the C_{3v} group that we have presented is said to have the coordinates x, y, and z as its *basis*. Other representations can be obtained by using other functions as a basis and determining how the symmetry operators change these functions. The matrices in a representation do not have to have any physical interpretation, but they must multiply in the same way as do the symmetry operators, must be square, and all must have the same number of rows and columns. In some representations, called *unfaithful* or *homomorphic*, there are fewer matrices than there are symmetry operators, so that one matrix represents two or more symmetry operators.

Group representations are divided into two kinds, *reducible* and *irreducible*. In a reducible representation, the matrices are "block-diagonal" or can be put into block-diagonal form by a *similarity transformation*. A similarity transformation means forming the matrix product

$$\mathbf{P} = \mathbf{X}^{-1}\mathbf{Q}\mathbf{X}, \qquad (13.73)$$

where $\mathbf{P}$, $\mathbf{X}$, and $\mathbf{Q}$ are square matrices. A *block-diagonal matrix* is one in which all elements are zero except those in square regions along the diagonal. The following block-diagonal matrix has two 2 by 2 blocks and a 1 by1 block

$$\begin{vmatrix} 1 & 2 & 0 & 0 & 0 \\ 3 & 2 & 0 & 0 & 0 \\ 0 & 0 & 4 & 3 & 0 \\ 0 & 0 & 3 & 3 & 0 \\ 0 & 0 & 0 & 0 & 2 \end{vmatrix}.$$

All the matrices in a reducible representation have the same size blocks in the same order. The representation of the group C_{3v} given in Eq. (13.72) is reducible, since each matrix has a 2 by 2 block and a 1 by 1 block. When two block-diagonal matrices with the same size blocks are multiplied together, the result is a matrix that is block-diagonal with the same size blocks in the same order. This is apparent in our representation of the C_{3v} group, since each product yields a member of the group, all of which have the same blocks in the same order.

Exercise 13.30. Show by matrix multiplication that two matrices with a 2 by 2 block and two 1 by 1 blocks produce another matrix with a 2 by 2 block and two 1 by 1 blocks when multiplied together.

Because of the way in which block-diagonal matrices multiply, each of the 2 by 2 blocks in the matrices in Eq. (13.72) forms another representation of the C_{3v} group.

When a reducible representation is written with its matrices in block-diagonal form, the block submatrices form irreducible representations, and the reducible representation is said to be the *direct sum* of the irreducible representations. Both the representations of the C_{3v} group obtained from the submatrices are irreducible. The 1 by 1 blocks form an unfaithful or homomorphic representation, in which every operator is represented by the 1 by 1 identity matrix. This one-dimensional representation is called the *totally symmetric representation*.

Exercise 13.31. Pick a few pairs of 2 by 2 submatrices from Eq. (13.72) and show that they multiply in the same way as the 3 by 3 matrices.

In any representation of a symmetry group, the trace of a matrix (the sum of the diagonal elements) is called the *character* of the corresponding operator for that representation. A list of the characters for the members of a given representation is called a *character table*.

Example 13.22. Construct the character table for the representation of the C_{3v} group in Eq. (13.72).

By adding up the traces, we find the character table.

$\widehat{E}$	$\widehat{C}_3$	$\widehat{C}_3^2$	$\hat{\sigma}_a$	$\hat{\sigma}_b$	$\hat{\sigma}_c$
3	0	0	1	1	1

The two irreducible representations of the C_{3v} group that we have obtained are said to be *nonequivalent*, since they have different dimensions. There are several theorems governing irreducible representations for a particular group.[9] These theorems can be used to determine that three irreducible representations of the C_{3v} group occur, and that their dimensions are 2, 1, and 1. The other one-dimensional representation is

$$\begin{aligned} \widehat{E} \leftrightarrow 1 \quad \widehat{C}_3 \leftrightarrow 1 \quad \widehat{C}_3^2 \leftrightarrow 1, \\ \hat{\sigma}_a \leftrightarrow -1 \quad \hat{\sigma}_b \leftrightarrow -1 \quad \hat{\sigma}_c \leftrightarrow -1. \end{aligned} \tag{13.74}$$

Exercise 13.32. Show that the 1 by 1 matrices (scalars) in Eq. (13.74) obey the same multiplication table as does the group of symmetry operators.

Group theory can be applied to several different areas of molecular quantum mechanics, including the symmetry of electronic and vibrational wave functions, normal modes of vibration, and the study of transitions between energy levels.[10] There is also a theorem which says that there is a correspondence between an energy level and some one of the irreducible representations of the symmetry group of the molecule, and that the degeneracy (number of states in the level) is equal to the dimension of that irreducible representation.

PROBLEMS

1. Find the following commutators, where $\mathrm{D}_x = \mathrm{d}/\mathrm{d}x$:

(a) $[\widehat{\mathrm{D}}_x, \sin(x)]$;
(b) $[\widehat{\mathrm{D}}_x^3, x]$;

2. Find the following commutators, where $\mathrm{D}_x = \mathrm{d}/\mathrm{d}x$:

(a) $[\widehat{\mathrm{D}}_x^3, x^2]$;
(b) $[\widehat{\mathrm{D}}_x^2, f(x)]$.

3. The components of the angular momentum correspond to the quantum-mechanical operators:

$$\widehat{L}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \quad \widehat{L}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right),$$
$$\widehat{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).$$

These operators do not commute with each other. Find the commutator $[\widehat{L}_x, \widehat{L}_y]$.

4. The Hamiltonian operator for a one-dimensional harmonic oscillator moving in the x direction is

$$\widehat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{kx^2}{2}.$$

Find the value of the constant a such that the function e^{-ax^2} is an eigenfunction of the Hamiltonian operator and find the eigenvalue E. The quantity k is the force constant, m is the mass of the oscillating panicle, and $\hbar$ is Planck's constant divided by 2π.

5. In quantum mechanics, the *expectation value* of a mechanical quantity is given by

$$\langle A \rangle = \frac{\int \psi^* \widehat{A} \psi \, \mathrm{d}x}{\int \psi^* \psi \, \mathrm{d}x},$$

where $\widehat{A}$ is the operator for the mechanical quantity and ψ is the wave function for the state of the system. The integrals are over all permitted values of the coordinates of the system. The expectation value is defined as the prediction of the mean of a large number of measurements of the mechanical quantity, given that the system is in the state corresponding to ψ prior to each measurement.

[9] Ira N. Levine, *Quantum Chemistry*, Vol. II, p. 389, Allyn & Bacon, Boston, 1970.

[10] See P. W. Atkins, J. dePaula, and R. Friedman, *Quanta, Matter, and Change,*W. H. Freeman, New York, 2009, p. 327ff.

For a particle moving in the x direction only and confined to a region on the x axis from $x = 0$ to $x = a$, the integrals are single integrals from 0 to a and $\hat{p}_x$ is given by $(\hbar/i)\partial/\partial x$. The wave normalized function is

$$\psi = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right).$$

Normalization means that the integral in the denominator of the expectation value expression is equal to unity.

(a) Show that this wave function is normalized.
(b) Find the expectation value of x.
(c) The operator corresponding to p_x is $\left(\frac{\hbar}{i}\right)\frac{\mathrm{d}}{\mathrm{d}x}$. Find the expectation value of p_x.
(d) Find the expectation value of p_x^2.

6. If $\widehat{A}$ is the operator corresponding to the mechanical quantity A and ϕ_n is an eigenfunction of $\widehat{A}$, such that

$$\widehat{A}\phi_n = a_n\phi_n$$

show that the expectation value of A is equal to a_n if the state of the system corresponds to ϕ_n. See Problem 5 for the formula for the expectation value.

7. If x is an ordinary variable, the Maclaurin series for $1/(1-x)$ is

$$\frac{1}{1-x} = 1 + x^2 + x^3 + x^4 + \cdots$$

If $\widehat{X}$ is some operator, show that the series

$$1 + \widehat{X} + \widehat{X}^2 + \widehat{X}^3 + \widehat{X}^4 + \cdots$$

is the inverse of the operator $1 - \widehat{X}$.

8. Find the result of each operation on the given point (represented by Cartesian coordinates):

(a) $\widehat{i}(2,4,6)$.
(b) $\widehat{C}_{2(y)}(1,1,1)$.

9. Find the result of each operation on the given point (represented by Cartesian coordinates):

(a) $\widehat{C}_{3(z)}(1,1,1)$.
(b) $\widehat{S}_{4(z)}(1,1,1)$.

10. Find the result of each operation on the given point (represented by Cartesian coordinates):

(a) $\widehat{C}_{2(z)}\hat{\imath}\hat{\sigma}_h(1,1,1)$.
(b) $\widehat{S}_{2(y)}\hat{\sigma}_h(1,1,0)$.

11. Find the result of each operation on the given point (represented by Cartesian coordinates):

(a) $\widehat{C}_{2(z)}\hat{\imath}(1,1,1)$.
(b) $\hat{\imath}\widehat{C}_{2(z)}(1,1,1)$.

12. Find the 3 by 3 matrix that is equivalent in its action to each of the symmetry operators:

(a) $\widehat{S}_{2(z)}$.
(b) $\widehat{C}_{2(x)}$.

13. Find the 3 by 3 matrix that is equivalent in its action to each of the symmetry operators:

(a) $\widehat{C}_{8(x)}$.
(b) $\widehat{S}_{6(x)}$.

14. Give the function that results if the given symmetry operator operates on the given function for each of the following:

(a) $\widehat{C}_{4(z)}x^2$.
(b) $\hat{\sigma}_h x\cos(x/y)$.

15. Give the function that results if the given symmetry operator operates on the given function for each of the following:

(a) $\hat{\imath}(x + y + z^2)$.
(b) $\widehat{S}_{4(x)}(x + y + z)$.

16. Find the matrix products. Use Mathematica to check your result.

(a) $\begin{bmatrix} 0 & 1 & 2 \\ 4 & 3 & 2 \\ 7 & 6 & 1 \end{bmatrix}\begin{bmatrix} 1 & 2 & 3 \\ 6 & 8 & 1 \\ 7 & 4 & 3 \end{bmatrix}$,

(b) $\begin{bmatrix} 6 & 3 & 2 & -1 \\ -7 & 4 & 3 & 2 \\ 1 & 3 & 2 & -2 \\ 6 & 7 & -1 & -3 \end{bmatrix}\begin{bmatrix} 4 & 7 & -6 & -8 \\ 3 & -6 & 8 & -6 \\ 2 & 3 & -3 & 4 \\ -1 & 4 & 2 & 3 \end{bmatrix}$.

17. Find the matrix products. Use Mathematica to check your result.

(a) $\begin{bmatrix} 3 & 2 & 1 & 4 \end{bmatrix}\begin{bmatrix} 1 & 2 & 3 \\ 0 & 3 & -4 \\ 1 & -2 & 1 \\ 3 & 1 & 0 \end{bmatrix}$,

(b) $\begin{bmatrix} 1 & 2 & 3 \\ 0 & 3 & -4 \\ 1 & -2 & 1 \\ 3 & 1 & 0 \end{bmatrix}\begin{bmatrix} 2 \\ 3 \\ 3 \end{bmatrix}$,

(c) $\begin{bmatrix} 6 & 3 & -1 \\ 7 & 4 & -2 \end{bmatrix} \begin{bmatrix} 1 & 4 & -7 & 3 \\ 2 & 5 & 8 & -2 \\ 3 & 6 & -9 & 1 \end{bmatrix}$.

18. Show that $(\mathbf{AB})\mathbf{C} = \mathbf{A}(\mathbf{BC})$ for the matrices:

$$\mathbf{A} = \begin{bmatrix} 0 & 1 & 2 \\ 3 & 1 & -4 \\ 2 & 3 & 1 \end{bmatrix} \quad \mathbf{B} = \begin{bmatrix} 3 & 1 & 4 \\ -2 & 0 & 1 \\ 3 & 2 & 1 \end{bmatrix} \quad \mathbf{C} = \begin{bmatrix} 0 & 3 & 1 \\ -4 & 2 & 3 \\ 3 & 1 & -2 \end{bmatrix}.$$

19. Show that $\mathbf{A}(\mathbf{B} + \mathbf{C}) = \mathbf{AB} + \mathbf{AC}$ for the example matrices in the previous problem.

20. Test the following matrices for singularity. Find the inverses of any that are nonsingular. Multiply the original matrix by its inverse to check your work. Use Mathematica to check your work.

(a) $\begin{bmatrix} 0 & 1 & 2 \\ 3 & 4 & 5 \\ 6 & 7 & 8 \end{bmatrix}$

(b) $\begin{bmatrix} 6 & 8 & 1 \\ 7 & 3 & 2 \\ 4 & 6 & -9 \end{bmatrix}$

21. Test the following matrices for singularity. Find the inverses of any that are nonsingular. Multiply the original matrix by its inverse to check your work. Use Mathematica to check your work.

(a) $\begin{bmatrix} 3 & 2 & -1 \\ -4 & 6 & 3 \\ 7 & 2 & -1 \end{bmatrix}$

(b) $\begin{bmatrix} 0 & 2 & 3 \\ 1 & 1 & 1 \\ 2 & 0 & 1 \end{bmatrix}$.

22. Find the matrix $\mathbf{P}$ that results from the similarity transformation

$$\mathbf{P} = \mathbf{X}^{-1}\mathbf{QX},$$

where

$$\mathbf{Q} = \begin{bmatrix} 1 & 2 \\ 2 & 1 \end{bmatrix}, \quad \mathbf{X} = \begin{bmatrix} 2 & 3 \\ 4 & 3 \end{bmatrix}.$$

23. The H_2O molecule belongs to the point group C_{2v}, which contains the symmetry operators $\widehat{E}, \widehat{C}_2, \hat{\sigma}_a$, and $\hat{\sigma}_b$, where the C_2 axis passes through the oxygen nucleus and midway between the two hydrogen nuclei, and where the σ_a mirror plane contains the three nuclei and the σ_b mirror plane is perpendicular to the σ_a mirror plane.

(a) Find the 3 by 3 matrix that is equivalent to each symmetry operator.

(b) Show that the matrices obtained in part (a) have the same multiplication table as the symmetry operators, and that they form a group. The multiplication table for the group was to be obtained in Problem 8.23.

24. The BF_3 molecule is planar with bond angles of 120°.

(a) List the symmetry operators that belong to this molecule. We place the molecule in the x–y plane with the boron atom at the origin and one of the fluorine atoms on the x axis. Call the fluorine atoms a, b, and c starting at the x axis and proceeding counterclockwise around the x–y plane. The symmetry elements are: a threefold rotation axis, three vertical mirror planes containing a fluorine atom, the horizontal mirror plane, and three twofold rotation axes containing a fluorine atom.

(b) Find the three-dimensional matrices corresponding to the operators:

(i) $\widehat{C}_{3(z)}$.
(ii) $\hat{\sigma}_a$.
(iii) $\widehat{C}_{2a}$.

(c) Find the following operator products:

(i) $\widehat{C}_{3(z)}\hat{\sigma}_a$.
(ii) $\hat{\sigma}_a\hat{\sigma}_h$.
(iii) $\widehat{C}_{3(z)}\widehat{C}_{2a}$.

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Chapter 14

The Solution of Simultaneous Algebraic Equations with More than Two Unknowns

Principal Facts and Ideas

- To solve for n variables, n independent and consistent equations are required.
- If you have more than n independent and consistent equations for n variables, the system is overdetermined and has no solution.
- Simultaneous linear inhomogeneous equations can be solved with various techniques, including elimination, use of Cramer's formula, and by matrix inversion.
- Linear homogeneous simultaneous equations have a nontrivial solution only when a certain dependence condition is met.

Objectives

After studying this chapter, you should be able to:

- solve any fairly simple set of several simultaneous linear equations by the method of elimination;
- solve a set of linear inhomogeneous simultaneous equations by Cramer's method and by matrix inversion;
- solve a set of linear homogeneous simultaneous equations using the dependence condition.

14.1 CRAMER'S RULE

Cramer's rule is a systematic method for solving linear inhomogeneous simultaneous equations. Consider the set of two linear inhomogeneous equations:

$$a_{11}x + a_{12}y = c_1, \tag{14.1}$$

$$a_{21}x + a_{22}y = c_2. \tag{14.2}$$

Written in matrix form these equations are

$$\mathbf{AX} = \mathbf{C}, \tag{14.3}$$

where $\mathbf{A}$ is a square matrix, and $\mathbf{X}$ and $\mathbf{C}$ are column vectors:

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}. \tag{14.4}$$

Exercise 14.1. Use the rules of matrix multiplication to show that Eq. (14.3) is identical with Eqs. (14.1) and (14.2).

Cramer's rule states that the solutions to this set of equations are equal to quotients of determinants:

$$x = \frac{\begin{vmatrix} c_1 & a_{12} \\ c_2 & a_{22} \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}}, \tag{14.5}$$

$$y = \frac{\begin{vmatrix} a_{11} & c_1 \\ a_{21} & c_2 \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}}. \tag{14.6}$$

In both quotients the denominator is the determinant of the matrix $\mathbf{A}$. In the numerator for x, the column of coefficients for x is replaced by the constant column vector $\mathbf{C}$, and in the

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expression for y, the column of coefficients for y is replaced by **C**.

Example 14.1. Use Cramer's rule to solve the simultaneous equations

$$4x + y = 14,$$
$$2x - 3y = 0,$$

$$x = \frac{\begin{vmatrix} 14 & 1 \\ 0 & -3 \end{vmatrix}}{\begin{vmatrix} 4 & 1 \\ 2 & -3 \end{vmatrix}} = \frac{-42}{-12-2} = 3, \tag{14.7}$$

$$y = \frac{\begin{vmatrix} 4 & 14 \\ 2 & 0 \end{vmatrix}}{\begin{vmatrix} 4 & 1 \\ 2 & -3 \end{vmatrix}} = \frac{-28}{-12-1} = 2. \tag{14.8}$$

Exercise 14.2. Use Cramer's rule to solve the simultaneous equations

$$4x + y = 21,$$
$$2x - 3y = -11.$$

If there are more than two variables and more than two linear inhomogeneous equations, Cramer's rule uses the same pattern. Consider a set of three equations

$$a_{11}x_1 + a_{12}x_2 + a_{13}x_3 = c_3, \tag{14.9a}$$
$$a_{21}x_1 + a_{22}x_2 + a_{23}x_3 = c_2, \tag{14.9b}$$
$$a_{31}x_1 + a_{32}x_2 + a_{33}x_3 = c_3. \tag{14.9c}$$

These equations can be written in matrix notation:

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} \tag{14.10}$$

or

$$\mathbf{AX} = \mathbf{C},$$

where **X** and **C** are the column vectors shown.

According to Cramer's rule the value of x_1 is given by

$$\boxed{x_1 = \frac{\begin{vmatrix} c_1 & a_{12} & a_{13} \\ c_2 & a_{22} & a_{23} \\ c_3 & a_{32} & a_{33} \end{vmatrix}}{\det(\mathbf{A})}}, \tag{14.11}$$

where det (**A**) is the determinant of the 3 by 3 matrix of the a coefficients. The determinant in the numerator is obtained by replacing the first column in the matrix of coefficients by the constants c_1, c_2, and c_3 (the column vector **C**). The value of x_2 is given by a similar expression with the second column in the determinant in the numerator replaced by the constants c_1, c_2, and c_3. The value of x_3 is given by an expression with the third column in the determinant replaced by the column vector **C**.

Example 14.2. Use Cramer's rule to find the value of x_1 that satisfies

$$\begin{bmatrix} 2 & 4 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} 21 \\ 4 \\ 10 \end{bmatrix},$$

$$x_1 = \frac{\begin{vmatrix} 21 & 4 & 1 \\ 4 & -1 & 1 \\ 10 & 1 & 1 \end{vmatrix}}{\begin{vmatrix} 2 & 4 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & 1 \end{vmatrix}} = \frac{21\begin{vmatrix} -1 & 1 \\ 1 & 1 \end{vmatrix} - 4\begin{vmatrix} 4 & 1 \\ 1 & 1 \end{vmatrix} + 10\begin{vmatrix} 4 & 1 \\ -1 & 1 \end{vmatrix}}{2\begin{vmatrix} -1 & 1 \\ 1 & 1 \end{vmatrix} - 1\begin{vmatrix} 4 &] \\ 1 & 1 \end{vmatrix} + 1\begin{vmatrix} 4 & 1 \\ -1 & 1 \end{vmatrix}}$$
$$= \frac{21(-1-1) - 4(4-1) + 10(4+1)}{2(-1-1) - (4-1) + (4+1)} = \frac{-4}{-2} = 2.$$

Exercise 14.3. Find the values of x_2 and x_3 for the previous example.

Cramer's rule for more than three linear inhomogeneous equations is analogous to this. We write the equations in matrix form

$$\mathbf{AX} = \mathbf{C}, \tag{14.12}$$

where the matrices now have more than three rows and columns.In order to have a solution, the matrix **A** must be square and have the same number of rows and columns as the column vectors **X** and **C** have rows. Let $\mathbf{A}_n$ be the matrix that is obtained from **A** by replacing the nth column by the column vector **C**. Cramer's rule is now written

$$\boxed{x_n = \frac{\det(\mathbf{A_n})}{\det(\mathbf{A})}}. \tag{14.13}$$

Exercise 14.4. Find the value of x_1 that satisfies the set of equations

$$\begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & 1 \\ 1 & 1 & -1 & 1 \\ 1 & 1 & 1 & -1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} = \begin{bmatrix} 10 \\ 6 \\ 4 \\ 1 \end{bmatrix}.$$

14.2 LINEAR DEPENDENCE AND INCONSISTENCY

In Chapter 5 we discussed linear dependence and inconsistency in the case of two equations. We will not present a complete discussion of consistency and independence for sets of more than two equations, but we will make the following comments, which apply to sets of n linear inhomogeneous equations in n unknowns:

1. A set of n equations is said to be *linearly dependent* if a set of constants $b_1, b_2, \ldots, b_n$, not all equal to zero, can be found such that if the first equation is multiplied by b_1, the second equation by b_2, the third equation by b_3, and so on, the equations add to zero for all values of the variables. A simple example of linear dependence is for two of the equations to be identical. In this case, we could multiply one of these equations by $+1$ and the other by -1 and all of the remaining equations by 0 and have the equations sum to zero.Another simple case occurs if every term in one equation is proportional to the corresponding term in another equation. If two equations are identical or proportional to each other, one has only $n-1$ usable equations and cannot solve for n variables. More complicated types of linear dependence also occur, and in any case one has only $n-1$ usable equations or fewer.
2. A set of equations is inconsistent if two or more of the equations correspond to incompatible solutions.
3. From Cramer's rule, you can see that if the determinant in the denominator vanishes, there is no solution to the set of equations. If there are two identical equations or two equations that are proportional to each other, the determinant of the matrix $\mathbf{A}$ vanishes, as seen from the properties of determinants described in Chapter 13. The determinant of $\mathbf{A}$ will also vanish in more complicated types of linear dependence. If $\det(\mathbf{A})$ vanishes, either the equations are linearly dependent or they are inconsistent.
4. A set of more than n equations for n variables is overdetermined if the equations are consistent and independent, and the set has no solution.
5. A set of more than n equations in n variables can be solved if some of the equations are linearly dependent.

Example 14.3. Determine whether the set of four equations in three unknowns can be solved:

$$\begin{aligned} x_1 + x_2 + x_3 &= 6, \\ x_1 + x_2 + x_3 &= 12, \\ 3x_1 + 3x_2 + x_3 &= 12, \\ 2x_1 + x_2 + 4x_3 &= 16. \end{aligned}$$

The first two equations are inconsistent, since 6 is not equal to 12. There is no solution to this set of equations.

Exercise 14.5. Determine whether the set of four equations in three unknowns can be solved:

$$\begin{aligned} x_1 + x_2 + x_3 &= 12, \\ 4x_1 + 2x_2 + 8x_3 &= 52, \\ 3x_1 + 3x_2 + x_3 &= 25, \\ 2x_1 + x_2 + 4x_3 &= 26. \end{aligned}$$

14.3 SOLUTION BY MATRIX INVERSION

We write a set of linear inhomogeneous equations in matrix form:

$$\boxed{\mathbf{AX} = \mathbf{C}}, \tag{14.14}$$

where $\mathbf{A}$ is now an n by n square matrix, $\mathbf{X}$ is an n by 1 column vector containing the symbols for the unknowns, and $\mathbf{C}$ is another n by 1 column vector containing constants, at least some of which must be nonzero. If we possess the inverse of $\mathbf{A}$, we can multiply both sides this equation on the left by $\mathbf{A}^{-1}$ to get

$$\boxed{\mathbf{A}^{-1}\mathbf{AX} = \mathbf{X} = \mathbf{A}^{-1}\mathbf{C}}. \tag{14.15}$$

The column vector $\mathbf{A}^{-1}\mathbf{C}$ contains the solutions.

In order for a matrix to possess an inverse, it must be *nonsingular*, which means that its determinant does not vanish. If the matrix is singular, the system of equations cannot be solved because it is either linearly dependent or inconsistent. We have already discussed the inversion of a matrix in Chapter 13. The difficulty with carrying out this procedure by hand is that it is probably more work to invert an n by n matrix than to solve the set of equations by other means. However, with access to Mathematica, BASIC, or another computer language that automatically inverts matrices, you can solve such a set of equations very quickly.

Example 14.4. Solve the following set of simultaneous equations by matrix inversion:

$$\begin{aligned} 2x_1 + x_2 &= 1, \\ x_1 + 2x_2 + x_3 &= 2, \\ x_2 + 2x_3 &= 3. \end{aligned}$$

The inverse of the relevant matrix has already been obtained in Chapter 13:

$$\begin{bmatrix} 2 & 1 & 0 \\ 1 & 2 & 1 \\ 0 & 1 & 2 \end{bmatrix}^{-1} = \begin{bmatrix} \frac{3}{4} & -\frac{1}{2} & \frac{1}{4} \\ -\frac{1}{2} & 1 & -\frac{1}{2} \\ \frac{1}{4} & -\frac{1}{2} & \frac{3}{4} \end{bmatrix},$$

$$\begin{bmatrix} \frac{3}{4} & -\frac{1}{2} & \frac{1}{4} \\ -\frac{1}{2} & 1 & -\frac{1}{2} \\ \frac{1}{4} & -\frac{1}{2} & \frac{3}{4} \end{bmatrix} \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} \\ 0 \\ \frac{3}{2} \end{bmatrix}.$$

The solution is

$$x_1 = \frac{1}{2}, \quad x_2 = 0, \quad x_3 = \frac{3}{2}.$$

Exercise 14.6. Solve the simultaneous equations by matrix inversion

$$\begin{aligned} 2x_1 + x_2 &= 4, \\ x_1 + 2x_2 + x_3 &= 7, \\ x_2 + 2x_3 &= 8. \end{aligned}$$

14.4 GAUSS–JORDAN ELIMINATION

This procedure is very similar to the Gauss–Jordan method for finding the inverse of a matrix, described in Chapter 13. If the set of equations is written in the vector form

$$\mathbf{AX} = \mathbf{C}.$$

We write an *augmented matrix* consisting of the **A** matrix and the **C** column vector written side by side. For a set of four equations, the augmented matrix is

$$\left[\begin{array}{cccc:c} a_{11} & a_{12} & a_{13} & a_{14} & c_1 \\ a_{21} & a_{22} & a_{23} & a_{24} & c_2 \\ a_{31} & a_{32} & a_{33} & a_{34} & c_3 \\ a_{41} & a_{42} & a_{42} & a_{44} & c_4 \end{array}\right]. \tag{14.16}$$

Row operations are carried out on this augmented matrix: a row can be multiplied by a constant, and one row can be subtracted from or added to another row. These operations will not change the roots to the set of equations, since such operations are equivalent to multiplying all terms of one equation by a constant or to taking the sum or difference of two equations. In Gauss–Jordan elimination, our aim is to transform the left part of the augmented matrix into the identity matrix, which will transform the right column into the four roots, since the set of equations will then be

$$\mathbf{EX} = \mathbf{C}' \tag{14.17}$$

and the solutions are contained in the column vector $\mathbf{C}'$. The row operations are carried out exactly as in Section 13.4 except for having only one column in the right part of the augmented matrix.

Exercise 14.7. Use Gauss–Jordan elimination to solve the set of simultaneous equations in the previous example. The same row operations will be required that were used in Example 13.10.

There is a similar procedure known as *Gauss elimination*, in which row operations are carried out until the left part of the augmented matrix is in upper triangular form. The bottom row of the augmented matrix then provides the root for one variable. This is substituted into the equation represented by the next-to-bottom row, and it is solved to give the root for the second variable. The two values are substituted into the next equation up, and so on.

14.5 LINEAR HOMOGENEOUS EQUATIONS

In Chapter 5 we discussed pairs of linear homogeneous equations for two variables. We found that such a pair of equations needed to be linearly dependent in order to have a solution other than the *trivial solution* $x = 0$, $y = 0$. A nontrivial solution consists of a formula giving one of the variables in terms of the other, since we essentially have only one independent equation. The same is true of sets with more than two variables. A set of three linear homogeneous equations in three unknowns is written

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + a_{13}x_3 &= 0, \\ a_{21}x_1 + a_{22}x_2 + a_{23}x_3 &= 0, \\ a_{31}x_2 + a_{32}x_2 + a_{33}x_3 &= 0. \end{aligned} \tag{14.18a}$$

If we attempt to apply Cramer's rule to this set of equations, without asking whether it is legitimate to do so, we find that

$$x_1 = \frac{\begin{vmatrix} 0 & a_{12} & a_{13} \\ 0 & a_{22} & a_{23} \\ 0 & a_{32} & a_{33} \end{vmatrix}}{\det(\mathbf{A})}. \tag{14.19}$$

If $\det(\mathbf{A}) \neq 0$, this yields $x_1 = 0$, and similar equations will also give $x_2 = 0$ and $x_3 = 0$. This trivial solution is all that we can have if the determinant of **A** is nonzero (i.e. if the three equations are independent and consistent). To have a nontrivial solution, the equations must be linearly dependent, which means that the condition

$$\det(\mathbf{A}) = 0 \tag{14.20}$$

must be satisfied. In the 3 by 3 case this condition is

$$\begin{aligned} &a_{11}a_{22}a_{33} - a_{11}a_{23}a_{32} - a_{12}a_{21}a_{33} - a_{13}a_{22}a_{31} \\ &\quad + a_{12}a_{23}a_{31} + a_{13}a_{21}a_{32} = 0. \end{aligned} \tag{14.21}$$

Example 14.5. Does the following set of equations have a nonzero solution?

$$\begin{aligned} x + y + z &= 0, \\ 2x + 3y + 4z &= 0, \\ 5x + 6y + 7z &= 0. \end{aligned}$$

If it does, find the solution.

The determinant of the coefficients is

$$\begin{vmatrix} 1 & 1 & 1 \\ 2 & 3 & 4 \\ 5 & 6 & 7 \end{vmatrix} = 1 \begin{vmatrix} 3 & 4 \\ 6 & 7 \end{vmatrix} - 1 \begin{vmatrix} 2 & 4 \\ 5 & 7 \end{vmatrix} + 1 \begin{vmatrix} 2 & 3 \\ 5 & 6 \end{vmatrix}$$
$$= 21 - 24 - 14 + 20 + 12 - 15 = 0.$$

The determinant vanishes, so the system can have a nontrivial solution set. The equations are linearly dependent, as can be seen from the fact that if the first equation is multiplied by 3 and added to the second equation, the result is the same as the third equation. We disregard the third equation and use the first equation to obtain

$$y = -x - z.$$

We replace y in the second equation by $-x - z$:

$$2x - 3(x + z) + 4z = 0,$$

which gives x in terms of z.

$$x = z.$$

We replace x by z in the second equation to find

$$2z + 3y + 4z = 0,$$

which gives y in terms of z.

$$y = -2z.$$

Exercise 14.8. Find expressions for x and y in terms of z for the set of equations

$$\begin{aligned} 2x + 3y - 12z &= 0, \\ x + y - z &= 0, \\ 2x - 3y &= 0. \end{aligned}$$

14.6 MATRIX EIGENVALUES AND EIGENVECTORS

One case in which a set of linear homogeneous equations arises is the *matrix eigenvalue problem*. This problem is very similar to an eigenvalue equation for an operator, as in Eq. (13.1). The problem is to find a column vector, $\mathbf{X}$ and a single scalar *eigenvalue* b, such that

$$\mathbf{BX} = b\mathbf{X}, \tag{14.22}$$

where $\mathbf{B}$ is the square matrix for which we want to find an eigenvector and $\mathbf{X}$ is the *eigenvector* (a column vector). Since the right-hand side of Eq. (14.22) is the same as $b\mathbf{EX}$ where $\mathbf{E}$ is the identity matrix, we can rewrite Eq. (14.22) as

$$(\mathbf{B} - b\mathbf{E})\mathbf{X} = 0, \tag{14.23}$$

which represents a set of linear homogeneous equations. The equations must be linearly dependent in order to have a solution.

Example 14.6. Find the values of b and $\mathbf{X}$ that satisfy the eigenvalue equation

$$\begin{bmatrix} 1 & 1 & 0 \\ 1 & 1 & 1 \\ 0 & 1 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = b \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}$$

and obey the normalization condition:

$$x_1^2 + x_2^2 + x_3^2 = 1.$$

Since the equations must be linearly dependent, the matrix equation can provide expressions for two of the variables in terms of the third variable, and the normalization condition will then provide unique values for the three variables.

The eigenvalue equation is equivalent to

$$\begin{bmatrix} 1-b & 1 & 0 \\ 1 & 1-b & 1 \\ 0 & 1 & 1-b \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = 0.$$

We let $y = 1 - b$. The equations must obey the condition

$$\begin{vmatrix} y & 1 & 0 \\ 1 & y & 1 \\ 0 & 1 & y \end{vmatrix} = y \begin{vmatrix} y & 1 \\ 1 & y \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 \\ 0 & y \end{vmatrix} = y^3 - 2y = 0.$$

This is a cubic equation that can be solved by factoring

$$y^3 - 2y = y\left(y - \sqrt{2}\right)\left(y + \sqrt{2}\right).$$

The three roots are

$$y = 0, \quad y = -\sqrt{2}, \quad y = \sqrt{2}$$

or

$$b = 1, \quad b = 1 - \sqrt{2}, \quad b = 1 + \sqrt{2}.$$

The three roots are three different eigenvalues. It is only when b is equal to one of these three values that the simultaneous equations have a nontrivial solution set.

Since we have three values of b, we have three different eigenvectors. We begin with $b = 1$:

$$\begin{aligned} 0 + x_2 + 0 &= 0, \\ x_1 + 0 + x_3 &= 0, \\ 0 + x_2 + 0 &= 0. \end{aligned}$$

It is now obvious that this set of equations is linearly dependent, as required, since the first and third equations are the same. Our solution is now

$$\begin{aligned} x_2 &= 0, \\ x_1 &= -x_3. \end{aligned}$$

We have solved for two of the variables in terms of the third. Since we have only two independent equations, we do not have definite values for x_1 and x_3. We impose the normalization condition and find

$$x_1 = 1/\sqrt{2}, \quad x_2 = 0, \quad x_3 = -1/\sqrt{2},$$

$$\mathbf{X} = \begin{bmatrix} 1/\sqrt{2} \\ 0 \\ -1/\sqrt{2} \end{bmatrix}.$$

The negative of this eigenvector could also have been taken.

We now seek the second eigenvector, for which $y = \sqrt{2}$, or $b = 1 - \sqrt{2}$. Substitution of this into the simultaneous equations gives

$$\begin{aligned} \sqrt{2}x_1 + x_2 + 0 &= 0, \\ x_1 + \sqrt{2}x_2 + x_3 &= 0, \\ 0 + x_2 + \sqrt{2}x_3 &= 0. \end{aligned}$$

The solution is

$$x_1 = x_3, \quad x_2 = -x_3\sqrt{2}.$$

With the normalization condition, the solution to this is

$$\mathbf{X} = \begin{bmatrix} 1/2 \\ -1/\sqrt{2} \\ 1/2 \end{bmatrix}.$$

Exercise 14.9. Show that the second eigenvector in the previous example is an eigenvector.

Exercise 14.10. Find the third eigenvector for the previous example.

In various methods in quantum chemistry, orbital functions are represented as linear combinations of basis functions. A set of linear homogeneous simultaneous equations arises that is to be solved for the coefficients in the linear combinations. The determinant condition is called a *secular equation*, and the eigenvalue represents the orbital energy. The simplest approximate theory using this representation for molecular orbitals is the Hückel method,[1] which is called a semi-empirical method because it relies on experimental data to evaluate certain integrals that occur in the theory. Certain other integrals are assumed to vanish.

Example 14.7. Obtain expressions for the orbital energies for the allyl radical CH_2CHCH_2 in the Hückel approximation.

The secular equation is

$$\begin{vmatrix} \alpha - W & \beta & 0 \\ \beta & \alpha - W & \beta \\ 0 & \beta & \alpha - W \end{vmatrix} = 0,$$

where W denotes the orbital energy and where α and β denote integrals whose values are to be deduced from experimental data. We divide all elements of the determinant by β and let $x = (\alpha - W)/\beta$ so that we have

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0.$$

Solving the secular equation determine the three orbital energies in terms of α and β.

$$\begin{aligned} \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} &= x \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - \begin{vmatrix} 1 & 0 \\ 1 & x \end{vmatrix} + 0 \\ &= x^3 - x - x + 0 = x^3 - 2x + 0 = 0. \end{aligned}$$

The solution set is

$$x = 0, \quad x = -\sqrt{2}, \quad x = \sqrt{2},$$

$$W = a - \sqrt{2}\beta, \quad a, \quad a + \sqrt{2}\beta.$$

Exercise 14.11. The Hückel secular equation for the hydrogen molecule is

$$\begin{vmatrix} \alpha - W & \beta \\ \beta & \alpha - W \end{vmatrix} = 0.$$

Determine the two orbital energies in terms of α and β.

[1] Donald J. Royer, *Bonding Theory*, pp. 154–163, McGraw–Hill, New York, 1968.

14.7 THE USE OF MATHEMATICA TO SOLVE SIMULTANEOUS EQUATIONS

In Chapter 5 we introduced the use of Mathematica to solve a single algebraic equation, using the *Solve* statement and the *NSolve* statement. The *Solve* statement can also be used to solve simultaneous equations. The equations are typed inside curly brackets with commas between them, and the variables are listed inside curly brackets. To solve the equations

$$ax + by = c,$$
$$gx + hy = k.$$

we type the input entry

```
Solve[{a x + b y == c, g x + h y == k}, {x,y}]
```

and press the "Enter" key. Notice the use of braces to notify Mathematica that we have a list of two equations and the use of the double equal sign. The output is

$$\text{Out[1]} = \left\{\left\{x -> ca + \frac{b(cg-ak)}{a(-(bg)+ah)}, y -> -\frac{(cg-ak}{-(bg)+ah)}\right\}\right\}.$$

To simplify the expressions for x and y, we use the fact that the percent symbol represents the last line of output and type

```
Simplify[%]
```

We receive the output

$$\text{Out[2]} = \left\{\left\{x -> \frac{-(ch)+bk}{bg-ah}, \quad y -> -\frac{-(cg)+ak}{-(bg)+ah}\right\}\right\},$$

which is the expression obtained from Cramer's rule.

The *Eliminate* statement is used to eliminate one or more of the variables in a set of simultaneous equations. For example, to obtain a single equation in x from the set of equations above, you would type the input entry (note the double equal signs):

```
Eliminate[{a x + by == c, g x + h y == k},y]
```

and would receive the output:

```
Out[1] = c h == b k − b g x + a h x.
```

We solve this equation for x by typing

```
Solve[%,x].
```

We receive the output:

$$\text{Out[2]} = \left\{\left\{x -> \frac{-(ch)+bk}{bg-ah}\right\}\right\}.$$

14.8 THE USE OF MATHEMATICA TO FIND MATRIX EIGENVALUES AND EIGENVECTORS

Mathematica finds matrix eigenvalues and eigenvectors by use of the statements *Eigenvalues[m]* and *Eigenvectors[m]*, where m denotes a matrix that has already been typed into the program.

Example 14.8. Use Mathematica to find the eigenvalues and eigenvectors of the matrix in the previous example.

We open Mathematica and type the input statement

```
m = {{1,1,0},{1,1,1},{0,1,1}}.
```

We press the "Enter" key and see the output

```
Out[1] = {{1,1,0},{1,1,1},{0,1,1}}.
```

We then type the statement

```
Eigenvalues[m].
```

We press the "Enter" key and see the output

$$\text{Out[2]} = \{1 + \sqrt{2}, 1, 1 - \sqrt{2}\}.$$

We type the statement

```
Eigenvectors[m]
```

and see the output

$$\text{Out[3]} = \{\{1, \sqrt{2}, 1\}, \{-1, 0, 1\}, \{1, \sqrt{2}, 1\}\}.$$

PROBLEMS

1. Solve the set of simultaneous equations:

$$3x + 4y + 5z = 1,$$
$$4x - 3y + 6z = 3,$$
$$7x + 2y - 6z = 2.$$

2. Solve the set of simultaneous equations:

$$y + z = 1,$$
$$x + z = 2,$$
$$x + y = 3.$$

3. Solve the set of equations, using Cramer's rule:

$$3x_1 + x_2 + x_3 = 19,$$
$$x_1 - 2x_2 + 3x_3 = 13,$$
$$x_1 + 2x_2 + 2x_3 = 23.$$

Verify your result using Mathematica.

4. Solve the set of equations, using Gauss–Jordan elimination:

$$x_1 + x_2 = 6,$$
$$2x_2 - x_3 = 1,$$
$$x_1 + 2x_2 = 5.$$

Use Mathematica to confirm your solution.

5. Solve the equation:

$$3x_1 + 4x_2 + 5x_3 = 25,$$
$$4x_1 + 3x_2 - 6x_3 = -7,$$
$$x_1 + x_2 + x_3 = 6.$$

6. Solve the equation:

$$\begin{bmatrix} 1 & 1 & 1 & 3 \\ 2 & 1 & 1 & 1 \\ 1 & 2 & 3 & 4 \\ 2 & 0 & 1 & 4 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} = \begin{bmatrix} 6 \\ 5 \\ 10 \\ 7 \end{bmatrix}.$$

7. Decide whether the following set of equations has a solution. Solve the equations if it does:

$$3x + 4y + z = 13,$$
$$4x + 3y + 2z = 10,$$
$$7x + 7y + 3z = 23.$$

8. Solve the set of equations by matrix inversion. If available, use Mathematica to invert the matrix:

$$2x_1 + 4x_2 + x_3 = 40,$$
$$x_1 + 6x_2 + 2x_3 = 55,$$
$$3x_1 + x_2 + x_3 = 23.$$

9. Find the eigenvalues and eigenvectors of the matrix

$$\begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix}.$$

10. Find the eigenvalues and eigenvectors of the matrix

$$\begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix}.$$

11. Find the eigenvalues and eigenvectors of the matrix

$$\begin{bmatrix} 1 & 0 & 1 \\ 1 & 0 & 1 \\ 1 & 0 & 1 \end{bmatrix}.$$

Does this matrix have an inverse?

12. In the Hückel treatment of the cyclopropenyl radical, the basis functions are the three 2pz atomic orbitals, which we denote by f_1, f_2, and f_3.

$$\psi = c_1 f_1 + c_2 f_2 + c_3 f_3.$$

The possible values of the orbital energy W are sought as a function of the c coefficients by solving the three simultaneous equations

$$xc_1 + c_2 + c_3 = 0,$$
$$c_1 + xc_2 + c_3 = 0,$$
$$c_1 + c_2 + xc_3 = 0,$$

where $x = (\alpha - W)/\beta$ and where α and β are certain integrals whose values are to be determined from empirical data.

(a) The determinant of the c coefficients must be set equal to zero in order for a nontrivial solution to exist. This is the *secular equation*. Solve the secular equation and obtain the orbital energies.

(b) Solve the three simultaneous equations, once for each value of x. Since there are only two independent equations, express c_2 and c_3 in terms of c_1.

(c) Impose the normalization condition

$$c_1^2 + c_2^2 + c_3^2 = 1$$

to find the values of the c coefficients for each value of W.

(d) Check your work by using Mathematica to find the eigenvalues and eigenvectors of the matrix

$$\begin{bmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{bmatrix}.$$

Chapter 15

Probability, Statistics, and Experimental Errors

Principal Facts and Ideas

- Every measured quantity is subject to experimental error.
- The two types of experimental errors are systematic errors and random errors.
- Systematic errors must usually be estimated by educated guesswork.
- Random errors are assumed to be a sample from a population of many imaginary replicas of the experiment.
- Such a population is assumed to be governed by probability theory.
- Mathematical statistics is used to infer the properties of a population from a sample.
- Random errors can be treated statistically if the measurement can be repeated a number of times.
- The mean of a set of repeated measurements is a better estimate of the correct value of a variable than is a single measurement.

Objectives

After studying the chapter, you should be able to:

- identify probable sources of error in a physical chemistry experiment and classify the errors as systematic or random;
- estimate systematic errors;
- understand the use of statistics to estimate random errors;
- calculate the mean and standard deviation of a sample of numbers;
- estimate the probable error in a measured quantity.

15.1 EXPERIMENTAL ERRORS IN MEASURED QUANTITIES

Every experimental measurement is subject to experimental error. If a measurement is repeated several times under the same conditions and if the repetitions agree closely with each other, the set of results is said to have good *precision*. If a measurement agrees well with the correct value, it is said to have good *accuracy*. It is tempting to assume that a set of measurements that has high precision also has high accuracy, but this can be a poor assumption.

15.1.1 Systematic and Random Errors

There are two principal types of experimental errors. *Systematic errors* recur with the same direction and with the same magnitude in every repetition of a measurement with the same procedure and apparatus. *Random errors* do not have the same direction and magnitude in every repetition. Systematic errors are generally produced by limitations in the apparatus used, whereas random errors can arise from limitations in the apparatus, limitations in the techniques, and unavoidable human error. Repetition of a measurement with the same apparatus and the same procedure does not provide information about systematic errors. Sometimes you can study systematic error by changing the design of the apparatus or by using a different apparatus. For example, an apparatus might include some insulation that minimizes unwanted heat transfer. If the measurement gives a different value when the insulation is improved, there was probably a systematic error at least as big as the change in the result. It is even better to make the measurement with different equipment in a different laboratory.

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00015-X

You can also study systematic errors by measuring a well-known quantity. For example, if you are measuring the melting temperature of an unknown substance, you could also measure the melting temperature of a known substance and compare your result with the accepted value. Any discrepancy could be due to systematic error, although if only one measurement is made you cannot separate the effects of systematic and random errors. These methods of estimating systematic errors are usually not available in physical chemistry laboratory courses. In this event, educated guesswork is nothing to be ashamed of.

If a measurement cannot be repeated, random errors must also be treated by educated guesswork. If a measurement can be repeated, information about random error can be obtained statistically. A set of such repeated measurements is considered to be a sample from a population of many imaginary repetitions of the measurement. Probability theory is used to study such a population. Statistics involves the analysis of the sample, and is used to infer the likely properties of the population.

Example 15.1. A primitive apparatus for measuring the melting temperature of a substance consists of a small bath containing a liquid in which the sample can be suspended in a small capillary tube held next to a thermometer. The bath is slowly heated and the thermometer reading at the time of melting of the sample is recorded. List some of the possible experimental error sources in this determination. Classify each as systematic or random and guess its relative magnitude.

- Faulty thermometer calibration. This is systematic. With an inexpensive thermometer, this error might be as large as several tenths of a degree.
- Lack of thermal equilibration between the liquid of the bath, the sample, and the thermometer. If the experimental procedure is the same for all repetitions, this will be systematic. If the thermometer is larger than the sample, it will likely be heated more slowly than the sample if the heating is done too rapidly. This error will probably be less than 1 °C.
- Failure to read the thermometer correctly. This is random. There are two kinds of errors here. The first is more of a blunder than an experimental error and amounts to counting the marks on the thermometer incorrectly and, for example, recording 87.5 °C instead of 88.5 °C. The other kind of error is due to *parallax*, or looking at the thermometer at some angle other than a right angle. This is a random error and might produce an error of about two-tenths of a degree Celsius.
- Presence of impurities in the sample. This is systematic, since impurities that dissolve in the liquid always lower the melting point. If carefully handled samples of purified substances are used, this error should be negligible.
- Failure to observe the onset of melting. This error is variable in magnitude, although always in the same direction. If the heating is done slowly, it should be possible to reduce this error to a few tenths of a degree.

Some of the errors in this example can be minimized by reducing the rate of heating. This suggests a possible procedure: an initial rough determination establishes the approximate value, and a final heating is done with slow and careful heating near the melting point.

Exercise 15.1. List as many sources of error as you can for some of the following measurements. Classify each one as systematic or random and estimate the magnitude of each source of error.

(a) The measurement of the diameter of a copper wire using a micrometer caliper.
(b) The measurement of the mass of a silver chloride precipitate in a porcelain crucible using a digital balance.
(c) The measurement of the resistance of an electrical heater using an electronic meter.
(d) The measurement of the time required for an automobile to travel the distance between two highway markers nominally 1 km apart, using a stopwatch.

15.2 PROBABILITY THEORY

Probability theory is the study of random events. The mathematical study of probability was begun by Pascal[1] and Fermat.[2] The principal applications of probability theory in physical chemistry are in the analysis of experimental errors and in quantum-mechanical theory. Probability theory begins with a large set of people, objects, or numbers, called a *population*. In the study of random experimental errors, the population is an imaginary set of infinitely many repetitions of a given measurement. In quantum mechanics, the population is an imaginary set of infinitely many replicas of the physical system, called an *ensemble*.

15.2.1 Properties of a Population

We focus on a numerical property and consider two different cases, the discrete case and the continuous case. In both

[1] Blaise Pascal (1623–1662) was a French mathematician and philosopher who became interested in probability when some gambler friends asked him how to predict the probable outcome of a game of chance that could not be finished.

[2] Pierre de Fermat (1601–1665) was a French lawyer and an amateur mathematician who is credited with founding the modern theory of numbers.

cases, the probability of a given occurrence is assumed to be governed by a probability distribution.

Discrete Probability Distributions

In this case a property of a member of a population can take on any one of a discrete set of values, such as $x_1, x_2, x_3, \ldots$ The probability that the value x_i will occur in a randomly chosen member of the population is assumed to be

$$\text{probability of } x_i = p_i. \tag{15.1}$$

The set of values $p_1, p_2, p_3, \ldots$ is a *discrete probability distribution*. All of these probabilities are required to be nonnegative (positive or zero). The sum of all of the probabilities is the *total probability*

$$p_{\text{tot}} = \sum_{i=1}^{\infty} p_i. \tag{15.2}$$

The most important property of a population of numerical values is its *mean value*. The mean is one of three commonly used averages. The other averages are the median and the mode. The *median* is defined such that half of the members of the population have a value greater than the median and half have a value smaller then the median. The *mode* is the most commonly occurring value in the population. The mean value of x for the distribution is denoted by $\langle x \rangle$ and is defined by

$$\langle x \rangle = \frac{1}{p_{\text{tot}}} \sum_{i=1}^{\infty} p_i x_i \text{ (definition of the mean value).} \tag{15.3}$$

If the probabilities are *normalized*, the total probability is set equal to unity:

$$\sum_{i=1}^{\infty} p_i = 1 \text{ (normalized probability distribution).} \tag{15.4}$$

With a normalized distribution the mean value is given by

$$\langle x \rangle = \sum_{i=1}^{\infty} p_i x_i \text{ (normalized probability distribution).} \tag{15.5}$$

Example 15.2. Find the probability of each of the outcomes of tossing two unloaded dice and find the mean value.

The outcomes range from 2 to 12. Here are the ways that each outcome can be obtained, and each of these ways is equally probable:

Total (n)	Ways to achieve	Number of ways	Normalized probability $= p_n$
2	1 and 1,	1	$1/36 = 0.02778$
3	1 and 2, 2 and 1	2	$2/36 = 0.05556$
4	1 and 3, 2 and 2, 3 and 1	3	$3/36 = 0.08333$
5	1 and 4, 2 and 3, 3 and 2, 4 and 1	4	$4/36 = 0.11111$
6	1 and 5, 2 and 4, 3 and 3, 4 and 2, 5 and 1	5	$5/36 = 0.13889$
7	1 and 6, 2 and 5, 3 and 4, 4 and 3, 5 and 2, 6 and 1	6	$6/36 = 0.16667$
8	2 and 6, 3 and 5, 4 and 4, 5 and 3, 2 and 6	5	$5/36 = 0.13889$
9	3 and 6, 4 and 5, 5 and 4, 6 and 3	4	$4/36 = 0.11111$
10	4 and 6, 5 and 5, 6 and 4	3	$3/36 = 0.08333$
11	5 and 6, 6 and 5	2	$2/36 = 0.05556$
12	6 and 6	1	$1/36 = 0.02778$

$$\begin{aligned}\langle n \rangle &= \sum_{n=2}^{12} p_n n \\ &= \left(\frac{1}{36}\right)(2) + \left(\frac{2}{36}\right)(3) + \left(\frac{3}{36}\right)(4) + \left(\frac{4}{36}\right)(5) \\ &\quad + \left(\frac{5}{36}\right)(6) + \left(\frac{6}{36}\right)(7) + \left(\frac{5}{36}\right)(8) + \left(\frac{4}{36}\right)(9) \\ &\quad + \left(\frac{3}{36}\right)(10) + \left(\frac{2}{36}\right)(11) + \left(\frac{1}{36}\right)(12) \\ &= 7.000.\end{aligned}$$

The distribution in this example is typical of many distributions in that it has a single peak with decreasing probabilities on either side of this peak.

One measure of the width of the peak is with the *variance*. The variance of a discrete distribution is denoted by σ^2 and is defined as the mean of the square of the deviation of the probabilities from the mean value:

$$\sigma_x^2 = \langle (x - \langle x \rangle)^2 \rangle = \sum_{i=1}^{N} p_i (x_i - \langle x \rangle)^2 \text{ (definition).} \tag{15.6}$$

Since the probabilities are all nonnegative (positive or zero), and since the other factor is squared, the variance cannot be negative. It is equal to zero only if all of the members of the population have the same value. We can obtain a more

convenient formula for the variance:

$$\begin{aligned}\sigma_x^2 &= \sum_{i=1}^{N}(x_i^2 - 2x_i\langle x\rangle + \langle x\rangle^2)p_i \\ &= \sum_{i=1}^{N} p_i x_i^2 - 2\sum_{i}^{N} p_i x_i\langle x\rangle + \langle x\rangle^2 \sum_{i}^{N} p_i \\ &= \langle x^2\rangle - 2\langle x\rangle^2 + \langle x\rangle^2(1) = \langle x^2\rangle - \langle x\rangle^2. \end{aligned} \quad (15.7)$$

Example 15.3. Find the variance for the distribution of dice throws in the previous example

$$\begin{aligned}\langle n^2\rangle &= \sum_{n=2}^{\infty} p_n n^2 \\ &= \left(\frac{1}{36}\right)(2^2) + \left(\frac{2}{36}\right)(3^2) + \left(\frac{3}{36}\right)(4^2) \\ &\quad + \left(\frac{4}{36}\right)(5^2) + \left(\frac{5}{36}\right)(6^2) + \left(\frac{6}{36}\right)(7^2) \\ &\quad + \left(\frac{5}{36}\right)(8^2) + \left(\frac{4}{36}\right)(9^2) + \left(\frac{3}{36}\right)(10^2) \\ &\quad + \left(\frac{2}{36}\right)(11^2) + \left(\frac{1}{36}\right)(12^2) \\ &= 54.8333 \end{aligned}$$

$$\sigma_n^2 = \langle n^2\rangle - \langle n\rangle^2 = 54.833 - 49.00 = 5.8333$$

The *standard deviation* is defined as the square root of the variance. For a general variable x,

$$\sigma_x = \left(\sigma_x^2\right)^{1/2} = [\langle x^2\rangle - \langle x\rangle^2]^{1/2} \text{ (definition)}. \quad (15.8)$$

The standard deviation for our dice throw example is equal to

$$\sigma_n = \sqrt{5.8333} = 2.415. \quad (15.9)$$

For most distributions with a single peak, about two-thirds of the members lie within one standard deviation of the mean. In this case, six of the 36 possible dice throws lie below 4.6 and six of the possible throws lie above 9.4, so that 24 of the throws (exactly two-thirds) lie within the range from $\langle n\rangle - \sigma_n$ and $\langle n\rangle + \sigma_n$.

The *binomial probability distribution* is an important example of a discrete distribution. Say that we toss an unbiased coin n times and want to find the probability that "heads" will come up m times. For a single toss, the probability of "heads" is equal to $1/2$. The probability that "heads" will come up every time on m consecutive throws is

$$\text{Probability} = \left(\frac{1}{2}\right)^m. \quad (15.10)$$

To analyze the probability that "heads" will come up m times out of n throws without regard to the order of the outcomes, let us imagine that n coins are laid out in a row and that each coin is tossed once. If m coins show "heads", the number of coins showing "tails" is $n - m$. The number of ways of arranging n coins along the row is called the number of *permutations* of n objects:

$$\begin{aligned}&\text{number of permutations of } n \text{ objects} = n! \\ &\quad = n(n-1)(n-2)(n-3)\cdots(3)(2)(1). \end{aligned} \quad (15.11)$$

The symbol $n!$ stands for *"n factorial"* and is defined by the second equality, except that 0! is defined to equal 1. You can see that this equality is correct by noting that you have n choices for placing the first coin, $n-1$ choices for the second coin, $n-2$ choices for the third coin, and so on.

If m of the coins are showing "heads," there are n choices to lay down the first "heads" coin, $n-1$ choices for the second "heads" coin, and so on down to coin number m. The number of ways to do this is

$$\text{Number of ways} = n(n-1)(n-2)\cdots n-m+1 = \frac{n!}{(n-m)!}. \quad (15.12)$$

However, the order of choosing the "heads" coins does not matter, so we must divide by $m!$, the number of permutations of the m "heads" coins. The number of ways of dividing the set of n coins into a set of m "heads" coins and $n-m$ "tails" coins is therefore

$$\text{Number of ways} = \frac{n!}{m!(n-m)!}. \quad (15.13)$$

This is the formula for the *binomial coefficient* since the formula for raising a polynomial to the nth power is

$$(x+y)^n = \sum_{m=0}^{n} \frac{n!}{m!(n-m)!} x^{n-m} y^m. \quad (15.14)$$

For example,

$$(x+y)^5 = x^5 + 5x^4y + 10x^3y^2 + 10x^2y^3 + 5xy^4 + y^5. \quad (15.15)$$

Since the probability of an unbiased coin coming up "heads" is equal to $1/2$ and the probability of the coin coming up "tails" is equal to $1/2$, the probability that m coins out of n coins coming up "heads" is

$$\begin{aligned}\text{Probability} &= \frac{n!}{m!(n-m)!}\left(\frac{1}{2}\right)^m\left(\frac{1}{2}\right)^{n-m} \\ &= \frac{n!}{m!(n-m)!}\left(\frac{1}{2}\right)^n. \end{aligned} \quad (15.16)$$

Example 15.4. Calculate the probability that "heads" will come up 50 times if an unbiased coin is tossed 100 times.

$$\begin{aligned}\text{Probability} &= \frac{100!}{50!50!}\left(\frac{1}{2}\right)^{100}\frac{9.3326\times10^{157}}{(3.0414\times10^{64})^2} \\ &\quad \times 7.8886\times10^{-31} = 0.07959. \end{aligned}$$

Exercise 15.2. Calculate the probability that "heads" will come up 60 times if an unbiased coin is tossed 100 times.

Exercise 15.3. Find the mean and the standard deviation for the distribution of "heads" coins in the case of 10 throws of an unbiased coin. Find the probability that a single toss will give a value within one standard deviation of the mean.

In the case of a biased coin, let p be the probability that "heads" will occur. The probability that "tails" will occur is equal to $1 - p$. The probability of "heads" coming up m times out of n throws is

$$\text{probability} = \frac{n!}{m!(n-m)!} p^m (1-p)^{n-m}. \tag{15.17}$$

This probability distribution is called the *binomial probability distribution*. Eq. (15.16) is the version for the case that $p = 1/2$. Figure 15.1 shows the binomial probability distribution for m "heads" outcomes out of 10 throws with an unbiased coin. This distribution has a single peak and resembles the familiar "bell-shaped" curve. The curve for larger values of n is even more nearly bell-shaped.

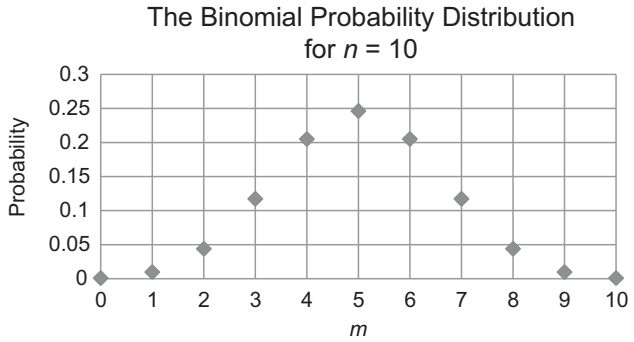

FIGURE 15.1 The binomial probability distribution for $n = 10$.

Continuous Probability Distributions

In this case, a numerical property of a member of a population can take on any value within a certain range. For a given independent variable (a *random variable*), x, we define a *continuous probability distribution* $f(x)$, or *probability density* such that

$$\text{probability of values of } x \text{ between } x' \text{ and } x' + \mathrm{d}x = f(x')\mathrm{d}x, \tag{15.18}$$

where $\mathrm{d}x$ is an infinitesimal range of values of x and x' is a particular value of x. The probability is proportional to $\mathrm{d}x$, so the function $f(x)$ depends on x but is independent of $\mathrm{d}x$. If c and d are two values of x within the range of possible values of x, the probability that x will lie between c and d is the integral

$$\text{probability that } c \prec x \prec d = \int_c^d f(x)\mathrm{d}x. \tag{15.19}$$

If $x_{\min}$ is the smallest possible value of x and $x_{\max}$ is the largest possible value of x, the total probability of all occurrences is given by

$$\text{total probability} = \int_{x_{\min}}^{x_{\max}} f(x)\mathrm{d}x. \tag{15.20}$$

If the probability distribution is *normalized*, the total probability is equal to unity:

$$\int_{x_{\min}}^{x_{\max}} f(x)\mathrm{d}x = 1 \text{ (normalized probability distribution).} \tag{15.21}$$

The mean value of x is given by

$$\boxed{\langle x \rangle = \frac{\displaystyle\int_{x_{\min}}^{x_{\max}} x f(x)\mathrm{d}x}{\displaystyle\int_{x_{\min}}^{x_{\max}} f(x)\mathrm{d}x}}. \tag{15.22}$$

We will frequently use the symbol μ to stand for a population mean value. If the probability distribution is normalized, the mean is given by

$$\mu = \langle x \rangle = \int_{x_{\min}}^{x_{\max}} x f(x)\mathrm{d}x \quad \text{(normalized probability distribution).} \tag{15.23}$$

Unless otherwise stated, we will assume that all probability distributions are normalized.

The *mean-square value* of x is given by

$$\langle x^2 \rangle = \int_{x_{\min}}^{x_{\max}} x^2 f(x)\mathrm{d}x. \tag{15.24}$$

The *root-mean-square value* of x is given by

$$x_{\text{rms}} = \langle x^2 \rangle^{1/2} = \left(\int_{x_{\min}}^{x_{\max}} x^2 f(x)\mathrm{d}x \right)^{1/2}. \tag{15.25}$$

The *variance* is defined by

$$\boxed{\sigma_x^2 = \textstyle\int_{x_{\min}}^{x_{\max}} (x-\mu)^2 f(x)\mathrm{d}x \text{ (definition)}}, \tag{15.26}$$

where we add a subscript x to remind us that x is the variable being discussed. The square root of the variance is called the *standard deviation*.

$$\sigma_x = \left(\int_{x_{\min}}^{x_{\max}} (x-\mu)^2 f(x)\mathrm{d}x \right)^{1/2} \text{ (definition).} \tag{15.27}$$

The variance and the standard deviation are measures of the spread of the distribution. For most distributions with a single peak, about two-thirds of the members of a population lie in the region between $\mu - \sigma_x$ and $\mu + \sigma_x$.

We can write a more convenient formula for the variance:

$$\sigma_x^2 = \int_{x_{\min}}^{x_{\max}} (x-\mu)^2 f(x)\mathrm{d}x = \int_{x_{\min}}^{x_{\max}} x^2 f(x)\mathrm{d}x - 2\mu \int_a^b x f(x)\mathrm{d}x + \mu^2 \int_{x_{\min}}^{x_{\max}} f(x)\mathrm{d}x.$$

The second integral on the right-hand side of this equation is equal to μ, and since we assume that the probability distribution is normalized, the third integral on the right-hand side is equal to unity, so that

$$\sigma_x^2 = \int_{x_{\min}}^{x_{\max}} (x-\mu)^2 f(x)\mathrm{d}x = \langle x^2\rangle - 2\mu^2 + \mu^2 = \langle x^2\rangle - \mu^2 = \langle x^2\rangle - \langle x\rangle^2. \quad (15.28)$$

15.2.2 The Uniform Probability Distribution

If all values of x in the region $(a \prec x \prec b)$ are equally probable and all other values have zero probability, this probability distribution is called the *uniform probability distribution.* In normalized form

$$f = \frac{1}{b-a}. \quad (15.29)$$

The mean is given by

$$\langle x\rangle = \int_a^b x\frac{1}{b-a}\mathrm{d}x = \frac{1}{b-a}\frac{1}{2}x^2\Big|_a^b = \frac{1}{2}\frac{1}{b-a}(b^2-a^2) = \frac{1}{2}\frac{1}{b-a}(b-a)(b+a) = \frac{1}{2}(b+a). \quad (15.30)$$

As expected, the mean lies at the center of the range $(a \prec x \prec b)$. The mean-square value of x is

$$\langle x^2\rangle = \int_a^b x^2\frac{1}{b-a}\mathrm{d}x = \frac{1}{b-a}\frac{1}{3}x^3\Big|_a^b = \frac{1}{3}\frac{1}{b-a}(b^3-a^3) = \frac{1}{3}\frac{1}{b-a}(b-a)(b^2+ab+a^2) = \frac{1}{3}(b^2+ab+a^2). \quad (15.31)$$

The root-mean-square value of x is

$$\langle x^2\rangle^{1/2} = \left[\frac{1}{3}(b^2+ab+a^2)\right]^{1/2}. \quad (15.32)$$

The variance is given by

$$\sigma_x^2 = \langle x^2\rangle - \langle x\rangle^2 = \frac{1}{3}(b^2+ab+a^2) - \frac{1}{4}(b^2+2ab+a^2) = \frac{1}{12}(b^2+a^2) - \frac{2}{12}ab = \frac{1}{12}(b-a)^2. \quad (15.33)$$

The standard deviation is

$$\sigma_x = \sigma_x^2 = \frac{1}{2\sqrt{3}}(b-a). \quad (15.34)$$

Example 15.5. Find the mean, the variance, and the standard deviation for a uniform probability distribution with $a = 0.00$ and $b = 10.00$. Find the probability that x lies between $\mu - \sigma_x$ and $\mu + \sigma_x$.

The mean value of x is

$$\langle x\rangle = \frac{1}{2}(10.00 + 0.00) = 5.00.$$

The variance is

$$\sigma_x^2 = \frac{1}{12}(10.00)^2 = \frac{100.0}{12} = 8.333.$$

The standard deviation is

$$\sigma_x = (8.333\cdots)^{1/2} = 2.88675\cdots.$$

The probability that x lies between $\mu - \sigma_x$ and $\mu + \sigma_x$ is

$$\text{Probability} = \frac{1}{10.00}\int_{2.113249}^{7.88675}\mathrm{d}x = 0.57735.$$

Our result is somewhat smaller than two-thirds because the values outside this range are more probable than with most distributions.

Exercise 15.4. If x ranges from 0.00 to 10.00 and if $f(x) = cx^2$, find the value of c so that $f(x)$ is normalized. Find the mean value of x, the root-mean-square value of x, and the standard deviation.

15.2.3 The Gaussian Distribution

The *Gaussian probability distribution* was introduced by Gauss[3] and is assumed to govern a variety of populations, including human IQ scores and many physical phenomena.[4] In normalized form the Gaussian distribution is

$$\boxed{f(x) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right]}, \quad (15.35)$$

[3] Karl Friedrich Gauss (1777–1855) was a famous German mathematician who was well known as a mathematical prodigy.

[4] It has been said that physicists believe in the Gaussian distribution because they think that mathematicians have established it theoretically, while mathematicians believe in it because they think that physicists have established it empirically.

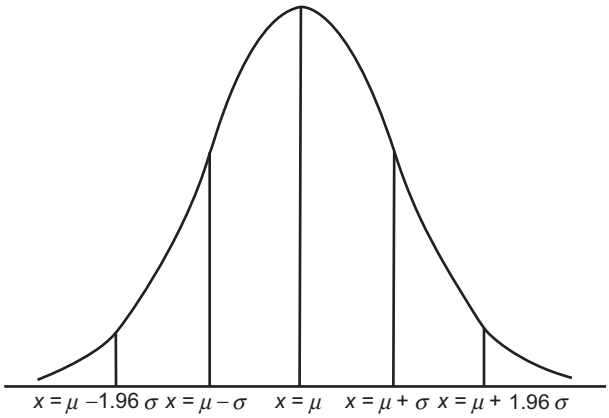

FIGURE 15.2 The Gaussian probability distribution.

where μ is the mean value and where σ is the standard deviation. All real values of x ranging from $-\infty$ to ∞ are included. The Gaussian distribution is also called the *normal distribution*. If $\sigma = 1$, then the distribution is called the *standard normal distribution*. Figure 15.2 shows a graph of the Gaussian distribution. Five values of x have been marked on the x axis: $x = \mu - 1.96\sigma$, $x = \mu - \sigma$, $x = \mu$, $x = \mu + \sigma$, and $x = \mu + 1.96\sigma$.

Example 15.6. Show that the Gaussian distribution in Eq. (15.35) satisfies the normalization condition.

We let

$$t = \frac{x-\mu}{\sqrt{2}\sigma},$$

$$\mathrm{d}x = \sqrt{2}\sigma\,\mathrm{d}t, \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}\sigma} e^{-(x-\mu)^2/2\sigma^2}\,\mathrm{d}x$$

$$= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-t^2}\,\mathrm{d}t = \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-t^2}\,\mathrm{d}t = 1.$$

We have looked up the integral in Appendix G.

Exercise 15.5. Calculate the mean and standard deviation of the Gaussian distribution, showing that μ is the mean and that σ is the standard deviation.

The Gaussian distribution conforms closely to the rule of thumb that two-thirds of the probability lies within one standard deviation of the mean:

$$\begin{aligned}(\text{fraction between } \mu-\sigma \text{ and } \mu+\sigma) &= \int_{\mu-\sigma}^{\mu+\sigma} \frac{1}{\sqrt{2\pi}\sigma} e^{-(x-\mu)^2/2\sigma^2}\mathrm{d}x \\ &= \int_{-\sigma}^{+\sigma} \frac{1}{\sqrt{2\pi}\sigma} e^{-y^2/2\sigma^2}\mathrm{d}y \\ &= \frac{2}{\sqrt{\pi}} \int_0^{1/\sqrt{2}} e^{-t^2}\mathrm{d}t. \end{aligned} \tag{15.36}$$

The last integral in this equation is the *error function* with argument $1/\sqrt{2}$. The integrand function e^{-t^2} does not possess an indefinite integral that can be written with a single formula, so the error function must be approximated numerically. The error function is described in Appendix G, which includes a table of values. From the table of values,

$$(\text{fraction between } \mu-\sigma \text{ and } \mu+\sigma) = \operatorname{erf}\left(\frac{1}{\sqrt{2}}\right) = \operatorname{erf}(0.707\cdots) = 0.683\cdots \tag{15.37}$$

For other intervals, we can write

$$(\text{fraction between } \mu-x_i \text{ and } \mu+x_i) = \operatorname{erf}\left(\frac{x_i}{\sqrt{2}\sigma}\right). \tag{15.38}$$

Example 15.7. Find the probability that x lies between $\mu - 0.500\sigma$ and $\mu + 0.500\sigma$ for a Gaussian distribution.

$$\text{Probability} = \frac{1}{\sqrt{2\pi}\sigma} \int_{\mu-0.500\sigma}^{\mu+0.500\sigma} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)\mathrm{d}x.$$

Since the integrand is an even function, we can write

$$\text{Probability} = \frac{2}{\sqrt{2\pi}\sigma} \int_{0}^{\mu+0.500\sigma} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)\mathrm{d}x.$$

We let

$$t = \frac{(x-\mu)}{\sqrt{2}\sigma}; \quad \mathrm{d}x = \sqrt{2}\sigma\,\mathrm{d}t,$$

$$\begin{aligned}\text{Probability} &= \sqrt{2}\sigma \frac{2}{\sqrt{2\pi}\sigma} \int_0^{0.500/\sqrt{2}} e^{-t^2}\mathrm{d}t \\ &= \frac{2}{\sqrt{\pi}} \int_0^{0.35355} e^{-t^2}\mathrm{d}t \\ &= \operatorname{erf}(0.35355) = 0.3829.\end{aligned}$$

You can show that 95% of the population lies within 1.96 standard deviations of the mean, and 99% of the population lies within 2.67 standard deviations of the mean.

Exercise 15.6. Show that the fraction of a population lying between $\mu - 1.96\sigma$ and $\mu + 1.96\sigma$ is equal to 0.950 for the Gaussian distribution.

The Gaussian distribution is generally assumed to govern random experimental errors. The *central limit theory of statistics* gives some justification for this assumption. This theorem states that if a number of *random variables* (independent variables) $x_1, x_2, \ldots, x_n$ are all governed by probability distributions with finite means

and finite standard deviations, then a *linear combination* (weighted sum)

$$y = \sum_{i=1}^{n} a_i x_i \tag{15.39}$$

is governed by a probability distribution that approaches a Gaussian distribution as n becomes large. If experimental errors arise from multiple sources, they should be at least approximately described by a Gaussian distribution.

15.2.4 Probability Distributions in Quantum Mechanics

According to quantum-mechanical theory, knowledge of the state of the system implies only that the wave function of the system is known. The value of mechanical variable such as the position of a particle is not necessarily precisely specified, but can be governed by a probability distribution. The probability distribution for the position of a particle is proportional to the square of the magnitude of the wave function. For example, the normalized wave function for the lowest-energy state of a particle in a one-dimensional "box" corresponding to $0 \prec x \prec L$ is

$$\psi = \sqrt{\frac{2}{L}} \sin(\pi x/L). \tag{15.40}$$

The normalized probability distribution for the particle's position is

$$f(x) = |\psi|^2 = \frac{2}{L} \sin^2(\pi x/L), \tag{15.41}$$

which is depicted in Figure 15.3

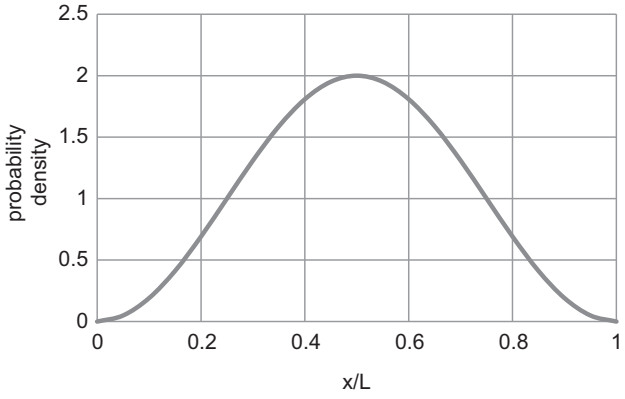

FIGURE 15.3 The square of the wave function of a particle in a box in its lowest-energy state.

For a given wave function, the predicted mean value of many measurements of a variable is called the *expectation value*. The expectation value of a variable A is given by

$$\langle A \rangle = \int \psi^* \widehat{A} \psi \, \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z, \tag{15.42}$$

where $\widehat{A}$ is the operator corresponding to the variable A, ψ is the wave function corresponding to the state of the system, and ψ^* is the complex conjugate of the wave function. For a particle moving only in the x direction, the expectation value of x is given by

$$\langle x \rangle = \int \psi^* x \psi \, \mathrm{d}x = \int x \psi^* \psi \, \mathrm{d}x = \int x |\psi|^2 \mathrm{d}x. \tag{15.43}$$

The spread of the distribution is given by the standard deviation:

$$\sigma_x = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2}. \tag{15.44}$$

Example 15.8. Find the expressions for $\langle x \rangle$ and σ_x for a particle in a box of length L in its lowest-energy state.

$$\begin{aligned}
\langle x \rangle &= \frac{2}{L} \int_0^L x \sin^2(\pi x/L) \mathrm{d}x \\
&= \frac{2}{L} \left(\frac{L}{\pi}\right)^2 \int_0^\pi y \sin^2(y) \mathrm{d}y \\
&= \left(\frac{2L}{\pi^2}\right) \left[\frac{y^2}{4} - \frac{y \sin(2y)}{4} - \frac{\cos(2y)}{8}\right]_0^\pi \\
&= \left(\frac{2L}{\pi^2}\right) \left(\frac{\pi^2}{4} - 0 - \frac{1}{8} - 0 + 0 + \frac{1}{8}\right) = \frac{L}{2}. \\
\langle x^2 \rangle &= \frac{2}{L} \int_0^L x^2 \sin^2(\pi x/L) \mathrm{d}x \\
&= \frac{2}{L} \left(\frac{L}{\pi}\right)^3 \int_0^\pi y^2 \sin^2(y) \mathrm{d}y \\
&= \left(\frac{2L^2}{\pi^3}\right) \left[\frac{y^3}{6} - \left(\frac{y^2}{4} - \frac{1}{8}\right)\right. \\
&\qquad \left. \times \sin(2y) - \frac{y \cos(2y)}{4}\right]_0^\pi \\
&= \left(\frac{2L^2}{\pi^3}\right) \left(\frac{\pi^3}{6}\right) = \frac{L^2}{3}. \\
\sigma_x &= (\langle x^2 \rangle - \langle x \rangle^2)^{1/2} \\
&= \left(\frac{L^2}{3} - \frac{L^2}{4}\right)^{1/2} = \left(\frac{L^2}{12}\right)^{1/2} \\
&= \frac{L}{\sqrt{12}} = 0.28868L.
\end{aligned}$$

Example 15.9. For a particle in a box, find the probability that the particle will be found within one standard deviation of the mean.

The probability is

$$\begin{aligned}
(\text{Probability}) &= \frac{2}{L} \int_{0.21132L}^{0.78868L} \sin^2(\pi x/L) \mathrm{d}x \\
&= \left(\frac{2}{L}\right)\left(\frac{L}{\pi}\right) \int_{0.66390}^{2.47770} \sin^2(y) \mathrm{d}y
\end{aligned}$$

$$
\begin{aligned}
&= \frac{2}{\pi}\left[\frac{y}{2} - \frac{\sin(y)\cos(y)}{2}\right]_{0.66390}^{2.47770} \\
&= \frac{2}{\pi}\left[\frac{2.47770}{2} - \frac{\sin(2.47770)\cos(2.47770)}{2}\right. \\
&\quad \left. - \frac{0.66390}{2} + \frac{\sin(0.66390)\cos(0.66390)}{2}\right] \\
&= \frac{2}{\pi}(1.23885 + 0.24265 \\
&\quad - 0.33195 + 0.24266) = 0.88631.
\end{aligned}
$$

This probability is somewhat larger than two-thirds since the probability density falls off strongly outside of this region.

Exercise 15.7. For the lowest-energy state of a particle in a box of length L, find the probability that the particle will be found between $L/4$ and $3L/4$.

The *Hamiltonian operator* is the operator corresponding to the energy. For a particle moving only in the x direction, it is given by

$$\widehat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \mathcal{V}(x), \tag{15.45}$$

where $\hbar$ is equal to Planck's constant divided by 2π and $\mathcal{V}(x)$ is the potential energy function.

Example 15.10. Find the expectation value of the energy and its standard deviation for the lowest-energy state of our particle in a box.

For the particle in a box, the constant potential energy $\mathcal{V}(x)$ is taken equal to zero.

$$
\begin{aligned}
\langle E\rangle &= -\frac{\hbar^2}{2m}\frac{2}{L}\int_0^L \sin(\pi x/L)\frac{\mathrm{d}^2}{\mathrm{d}x^2}\sin(\pi x/L) \\
&= \left(\frac{\pi}{L}\right)^2\frac{\hbar^2}{2m}\frac{2}{L}\int_0^L \sin^2(\pi x/L)\mathrm{d}x \\
&= \left(\frac{\pi}{L}\right)^2\frac{\hbar^2}{2m}\frac{2}{L}\frac{L}{\pi}\int_0^\pi \sin^2(u)\mathrm{d}u \\
&= \left(\frac{\pi}{L}\right)^2\frac{\hbar^2}{2m}\frac{2}{L}\frac{L}{\pi}\left[\frac{u}{2} - \frac{\sin(2u)}{4}\right]\Bigg|_0^\pi \\
&= \left(\frac{\pi}{L}\right)^2\frac{\hbar^2}{2m}\frac{2}{L}\frac{L}{\pi}\frac{\pi}{2} = \frac{\pi^2\hbar^2}{2mL^2} = \frac{h^2}{8mL^2}.
\end{aligned}
$$

The mean-square value of the energy is given by

$$
\begin{aligned}
\langle E^2\rangle &= \left(\frac{\hbar^2}{2m}\right)^2\frac{2}{L}\int_0^L \sin(\pi x/L)\frac{\mathrm{d}^4}{\mathrm{d}x^4}\sin(\pi x/L)\mathrm{d}x \\
&= \left(\frac{\pi}{L}\right)^4\left(\frac{\hbar^2}{2m}\right)^2\frac{2}{L}\int_0^L \sin^2(\pi x/L) \\
&= \left(\frac{\pi}{L}\right)^4\left(\frac{\hbar^2}{2m}\right)^2\frac{2}{L}\frac{L}{2} = \left(\frac{\pi^2\hbar^2}{2mL^2}\right)^2 = \left(\frac{h^2}{8mL^2}\right)^2.
\end{aligned}
$$

The standard deviation vanishes:

$$
\begin{aligned}
\sigma_E &= (\langle E^2\rangle - \langle E\rangle^2)^{1/2} \\
&= \left[\left(\frac{h^2}{8mL^2}\right)^2 - \left(\frac{h^2}{8mL^2}\right)^2\right]^{1/2} = 0.
\end{aligned}
$$

This vanishing value of the standard deviation indicates that the outcome of a measurement of the energy is precisely predictable if the state of the system corresponds to this wave function.

For a particle moving only in the x direction, the operator corresponding to the momentum is given by

$$\widehat{p}_x \leftrightarrow \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x} \tag{15.46}$$

and the operator corresponding to the square of the momentum is given by

$$\widehat{p_x^2} \leftrightarrow -\hbar^2\frac{\mathrm{d}^2}{\mathrm{d}x^2}. \tag{15.47}$$

Exercise 15.8. Find the expectation values for p_x and p_x^2 for the lowest-energy state of our particle in a box of length L. Find the standard deviation.

15.2.5 Probability Distributions in Gas Kinetic Theory

In elementary gas kinetic theory, a gas is modeled as a collection of many randomly moving noninteracting molecules. Each molecule is assumed to obey classical mechanics with its state specified by its position and velocity. We treat the molecules in a gas as a population. The distribution for the x component of the velocity of a molecule is the following Gaussian distribution:

$$f(v_x) = \left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{1/2}\exp\left(-\frac{mv_x^2}{2k_\mathrm{B}T}\right), \tag{15.48}$$

where m is the molecular mass, T is the temperature on the Kelvin scale, and k_B is Boltzmann's constant, equal to $1.3806568 \times 10^{-23}$ J K^{-1}. Figure 15.4 shows this probability distribution for nitrogen molecules at a temperature of 298.15 K.

Example 15.11. Show that the mean value of v_x is equal to zero:

$$\langle v_x\rangle = \left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{1/2}\int_{-\infty}^{\infty} v_x\exp\left(-\frac{mv_x^2}{2k_\mathrm{B}T}\right)\mathrm{d}v_x = 0.$$

The integrand is the product of an odd function, v_x, and an even function, $\exp\left(-\frac{mv_x^2}{2k_\mathrm{B}T}\right)$, so it is an odd function and

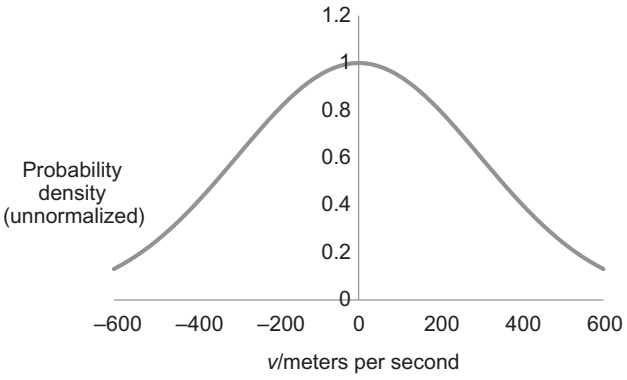

FIGURE 15.4 The probability distribution for the v_x component of the velocity for nitrogen molecules at a temperature of 298.15 K.

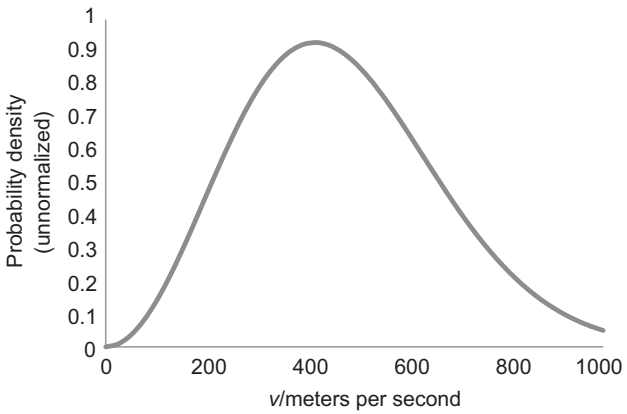

FIGURE 15.5 The probability density for speeds of nitrogen molecules at 298.15 K.

the integral vanishes. The physical reason for this vanishing property is that for any magnitude of v_x there is equal probability of moving from left to right (positive v_x) or from right to left (negative v_x).

Exercise 15.9. Find the expression for $\langle v_x^2 \rangle^{1/2}$, the root-mean-square value of v_x, and the expression for the standard deviation of v_x.

The y and z components of the velocity are analogous to the x component. The three-dimensional velocity $\mathbf{v}$ is given by

$$\mathbf{v} = \mathbf{i}v_x + \mathbf{j}v_y + \mathbf{k}v_z, \tag{15.49}$$

where $\mathbf{i}$,$\mathbf{j}$, and $\mathbf{k}$ are the unit vectors discussed in Chapter 4. The probability distribution for the velocity is

$$f(\mathbf{v}) = f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right). \tag{15.50}$$

The speed v is the magnitude of the velocity:

$$v = \sqrt{v_x + v_y + v_z}. \tag{15.51}$$

Since velocities with the same magnitude but different directions are included in the same speed, the distribution of speeds is different from the velocity distribution of Eq. (15.48). We denote the speed distribution by $f_v(v)$. It is given by

$$f_v(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right). \tag{15.52}$$

A graph of this function is shown in Figure 15.5. The speed is never negative, so the graph does not extend to the left of the origin. In ordinary gas kinetic theory, the requirements of special relativity are ignored, and speeds greater than the speed of light are included. The error due to this inclusion is insignificant at ordinary temperatures, because of the low probability ascribed to high speeds.

The mean speed is given by

$$\begin{aligned}\langle v \rangle &= \int_0^\infty v f_v(v) \mathrm{d}v \\ &= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty v^3 \exp\left(-\frac{mv^2}{2k_B T}\right) \mathrm{d}v \\ &= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \frac{(2k_B T)^2}{2m^2} \\ &= \left(\frac{8k_B T}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}. \end{aligned} \tag{15.53}$$

We have used Eq. (G.6) of Appendix G. In the last version of this equation we have used the fact that the molar mass M is equal to the molecular mass m times Avogadro's constant and that the ideal gas constant R is equal to Boltzmann's constant k_B times Avogadro's constant.

Exercise 15.10. Evaluate $\langle v \rangle$ for N_2 gas at 298.15 K.

Example 15.12. Find a formula for the mean of the square of the speed and the root-mean-square speed of molecules in a gas:

$$\begin{aligned}\langle v^2 \rangle &= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty v^4 \exp\left(-\frac{mv^2}{2k_B T}\right) \mathrm{d}v \\ &= \frac{3k_B T}{m} = \frac{3RT}{M}. \end{aligned}$$

The root-mean-square speed is

$$v_{\mathrm{rms}} = \langle v^2 \rangle^{1/2} = \left(\frac{3k_B T}{m}\right)^{1/2} = \left(\frac{3RT}{M}\right)^{1/2}.$$

The standard deviation is

$$\sigma_v^2 = \langle v^2 \rangle - \langle v \rangle^2 = \frac{3RT}{M} - \frac{8RT}{\pi M}$$
$$= \frac{RT}{M}\left(3 - \frac{8}{\pi}\right) = 0.4535\left(\frac{RT}{M}\right).$$

Exercise 15.11. Evaluate v_{rms} for N_2 gas at 298.15 K.

To find a formula for the most probable speed, we find the point at which the first derivative of $f_v(v)$ vanishes. We ignore the constant factor and write

$$\frac{\mathrm{d}}{\mathrm{d}v}\left[v^2 \exp\left(-\frac{mv^2}{2k_\mathrm{B}T}\right)\right]$$
$$= 2v \exp\left(-\frac{mv^2}{2k_\mathrm{B}T}\right)$$
$$-v^2 \exp\left(-\frac{mv^2}{2k_\mathrm{B}T}\right)\left(\frac{mv}{k_\mathrm{B}T}\right) = 0. \quad (15.54)$$

Dividing out the common factor, we obtain the expression

$$v_{\text{mp}}^2 = \frac{2k_\mathrm{B}T}{m},$$
$$v_{\text{mp}} = \left(\frac{2k_\mathrm{B}T}{m}\right)^{1/2} = \left(\frac{2RT}{M}\right)^{1/2}. \quad (15.55)$$

The most probable speed is smaller than the mean speed, which is smaller than the root-mean-square speed.

Exercise 15.12. Evaluate the most probable speed for nitrogen molecules at 298.15 K.

15.2.6 Time Averages

If h is a function of time, the time average of h over the time interval from t_1 to t_2 is defined as

$$\overline{h(t)} = \int_{t_1}^{t_2} h(t) f(t) \mathrm{d}t \text{ (weighted time average)} \quad (15.56)$$

The factor $f(t)$ is called a *weighting function*. It specifies the importance of different times in the time average. Most time averages are unweighted, which means that $f(t)$ is equal to $1/(t_2 - t_1)$:

$$\overline{h(t)} = \frac{1}{t_2 - t_1}\int_{t_1}^{t_2} h(t)\mathrm{d}t \text{ (unweighted time average).} \quad (15.57)$$

Equation (15.57) is a version of the *mean value theorem* of integral calculus, which states that the mean value of a function is equal to the integral of the function divided by the length of the interval over which the integral is taken.

Example 15.13. A particle falls in a vacuum near the surface of the earth. Find the time-average z component of the velocity during the first 1.00 s of fall if the initial speed is zero.

The velocity is given by

$$v_z = -gt,$$

where g is the acceleration due to gravity, equal to 9.80 m s^{-2}.

$$\overline{v_z} = -\frac{1}{1.00\text{ s}}\int_0^{1.00} gt\,\mathrm{d}t = -\left(\frac{g}{1.00\text{ s}}\right)\left[\frac{t^2}{2}\right]_0^{1.00}$$
$$= -\left(\frac{g}{1.00\text{ s}}\right)\left(\frac{1.00\text{ s}}{2}\right) = -(0.500\text{ s})g$$
$$= -(0.500\text{ s})\left(9.80\text{ m s}^{-2}\right) = -4.90\text{ m s}^{-1}.$$

Exercise 15.13. Find the value of the z coordinate after 1.00 s and find the time-average value of the z coordinate of the particle in the previous example for the first 1.00 s of fall if the initial position is $z = 0.00$ m.

15.3 STATISTICS AND THE PROPERTIES OF A SAMPLE

We consider a set of N repetitions of an experimental measurement to be a sample selected randomly from a large population of many imaginary repetitions of the measurement. The most important properties of a sample are its mean and its standard deviation. For a sample of N measurements, the *sample mean* is defined by

$$\boxed{\langle x \rangle = \frac{1}{N}\sum_{i=1}^{N} x_i \text{ (definition)}}, \quad (15.58)$$

where $x_1, x_2, \ldots$ are the members of the set. Mathematicians have shown that the sample mean is an unbiased estimate of the population mean.

Exercise 15.14. A sample of seven individuals has the following set of annual incomes: \$40,000, \$41,000, \$41,000, \$62,000, \$65,000, \$125,000, and \$650,000. Find the mean income, the median income, and the mode of this sample.

The *sample variance* is defined by

$$\boxed{s_x^2 = \frac{1}{N-1}\sum_{i=1}^{N}(x_i - \langle x \rangle)^2 \text{ (definition)}}. \quad (15.59)$$

We use the symbol s_x^2 for a sample variance and the symbol σ_x^2 for a population variance. Statisticians have shown that if we use the $N - 1$ denominator in Eq. (15.59) then the sample variance s_x^2 is an unbiased estimate of the population

variance σ_x^2. The use of the $N-1$ divisor has to do with the fact that in a sample of N members, there are N independent pieces of information, which can taken to be $N-1$ independent pieces of information in addition to the mean. We say that there are $N-1$ *degrees of freedom* in addition to the mean.[5] The symbol ν (Greek nu) is sometimes used for the number of degrees of freedom.

The *sample standard deviation* is the square root of the variance:

$$\boxed{s_x = \left(\frac{1}{N-1} \sum_{i=1}^{N} (x_i - \langle x \rangle)^2 \right)^{1/2} \quad \text{(definition)}}. \tag{15.60}$$

The standard deviation vanishes only if every member of the sample is equal to the sample mean, and otherwise must be positive. In most cases, about two-thirds of the members of a sample will have values between $\langle x \rangle - s_x$ and $\langle x \rangle + s_x$.

Example 15.14. Find the mean and the standard deviation of the set of numbers

$$32.41, \quad 33.76, \quad 32.91, \quad 33.04, \quad 32.75, \quad 33.23,$$

$$\begin{aligned} \langle x \rangle &= \frac{1}{6}(32.41 + 33.76 + 32.91 + 33.04 \\ &\quad + 32.75 + 33.23) = 33.02, \\ s_x &= \left\{ \frac{1}{5}[(0.39)^2 + (0.74)^2 + (-0.11)^2 \right. \\ &\quad \left. + (0.02)^2 + (0.27)^2 + (0.21)^2] \right\}^{1/2} \\ &= 0.41. \end{aligned}$$

One of the six numbers lies below 32.61, and one lies above 33.43, so that two-thirds of them lie between $\langle x \rangle - s_x$ and $\langle x \rangle + s_x$.

Exercise 15.15. Find the mean and the sample standard deviation for the following set of values: 2.876 m, 2.881 m, 2.864 m, 2.879 m, 2.872 m, 2.889 m, 2.869 m. Determine how many values lie below $\langle x \rangle - s_x$ and how many lie above $\langle x \rangle + s_x$.

15.4 NUMERICAL ESTIMATION OF RANDOM ERRORS

A standard practice is to make statements about errors that have a 95% probability of being correct. Such a statement is said to be at the 95% *confidence level*. For example, if the correct value of a quantity x is equal to μ, we want to make a statement of the form

$$\langle x \rangle - \varepsilon \prec \mu \prec \langle x \rangle + \varepsilon \tag{15.61}$$

that has a 95% chance of being correct. That is, we want to assert that the interval $\langle x \rangle - \varepsilon < x < \langle x \rangle + \varepsilon$ has a 95% chance of containing the correct value. We call such an interval the 95% *confidence interval* and we call the positive number ε the *probable error at the* 95% *confidence level* or the *estimated error*. If the population of imaginary replications of the measurement is governed by a Gaussian distribution and if we knew the value of σ, we could make this statement after a single measurement. We could say with 95% confidence that

$$x - 1.96\sigma \prec \mu \prec x + 1.96\sigma, \tag{15.62}$$

where x is the outcome of the measurement and μ is the correct value. However, we almost never have any information about the value of σ. If we have no opportunity to repeat our measurement, it is reasonable to make an educated guess of the value of σ.

If we make N measurements under the same conditions, we think of our set of N measurements as one possible set of N measurements from a population of many sets of measurements with N measurements in each set. We now have defined two populations: the original population of many repetitions of the measurement and the population of many sets of N repetitions of the measurement. If the original population is governed by a Gaussian distribution, mathematicians have shown that the sample means of the different sets of N measurements will be governed by a Gaussian distribution. The mean of this new population of sets of measurements is the same as the mean of the original population, and σ_m, the standard deviation of the sample means, is given by

$$\sigma_m = \frac{\sigma}{\sqrt{N}}, \tag{15.63}$$

where σ is the standard deviation of the original population. The new population of sample means has a smaller spread than the original population, and its spread becomes smaller as N becomes larger. That is, the means of the sets of measurements cluster more closely about the correct value than do individual measurements. If $N = 10$, $\sigma_m = 0.3162\sigma$ and if $N = 100$, $\sigma_m = 0.100\sigma$. Most people intuitively accept the notion that the average of a set of measurements is more likely to be closer to the correct value than is a single measurement and that the likelihood increases with an increase in the number of measurements.

If we knew the standard deviation of the original population, we would now be able to write an expression for the expected error in the mean of a set of N measurements:

$$\varepsilon = 1.96\sigma_m = \frac{1.96\sigma}{\sqrt{N}}. \tag{15.64}$$

[5] These $N-1$ degrees of freedom were illustrated once in a physical chemistry class that included one student who did not want the other students to know her score on an examination. The other students took their scores and the announced mean score and calculated the score of the first student.

However, we almost never know the population standard deviation. If we use the sample standard deviation as our estimate of the population standard deviation, we could write as a first approximation

$$\varepsilon = \frac{1.96 s_x}{\sqrt{N}} \text{ (first approximation)}, \tag{15.65}$$

where s is the sample standard deviation. However, this formula gives an underestimation of the error. A better formula was derived by Gossett,[6] who defined the *Student t factor*

$$t = \frac{(\langle x \rangle - \mu) N^{1/2}}{s_x}, \tag{15.66}$$

where μ is the population mean, $\langle x \rangle$ is the sample mean, and s_x is the sample standard deviation. There is a different value of t for every sample size. Although μ is not known, Gossett derived the probability distribution that t obeys.[7] From this distribution, which is called *Student's t distribution*, the maximum value of t corresponding to a given confidence level can be calculated for any value of N. The notation used for the 95% confidence level is $t(\nu,0.05)$, where ν is the number of degrees of freedom, equal to $N-1$. Unfortunately, some authors use a different notation for the critical value of t, such as $t_\nu(0.025)$, to represent the Student t factor for $\nu + 1$ data points at the 95% confidence level.[8] Table 15.1 gives these values for various values of N and for four different confidence levels. Notice that as N becomes large the maximum Student t value for 95% confidence (also called 0.05 significance) approaches 1.96.

Using a value from Table 15.1, we can write a formula for the expected error in the mean at the 95% confidence level

$$\boxed{\varepsilon = \frac{t(\nu,0.05) s_x}{\sqrt{N}}}, \tag{15.67}$$

where s_x is our sample standard deviation.

Example 15.15. Assume that the melting temperature of calcium nitrate tetrahydrate, $Ca(NO_3)_2 \cdot 4H_2O$, has been measured 10 times, and that the results are 42.70 °C, 42.60 °C, 42.78 °C, 42.83 °C, 42.58 °C, 42.68 °C, 42.65 °C, 42.76 °C, 42.73 °C, and 42.71 °C. Ignoring systematic errors, determine the 95% confidence interval for the set of measurements.

The sample mean melting temperature is:

$$\begin{aligned}\langle T_{\text{melt}} \rangle &= \frac{1}{10}(42.70\ ^\circ\text{C} + 42.60\ ^\circ\text{C} + 42.78\ ^\circ\text{C} \\ &\quad + 42.83\ ^\circ\text{C} + 42.58\ ^\circ\text{C} + 42.68\ ^\circ\text{C} + 42.65\ ^\circ\text{C} \\ &\quad + 42.76\ ^\circ\text{C} + 42.73\ ^\circ\text{C} + 42.71\ ^\circ\text{C}) \\ &= 42.70\ ^\circ\text{C}.\end{aligned}$$

The sample standard deviation is

$$\begin{aligned}s_T &= \left\{\frac{1}{9}[(0.00\ ^\circ\text{C})^2 + (0.10\ ^\circ\text{C})^2 + (0.08\ ^\circ\text{C})^2 \right. \\ &\quad + (0.13\ ^\circ\text{C})^2 + (0.12\ ^\circ\text{C})^2 + (0.02\ ^\circ\text{C})^2 \\ &\quad + (0.05\ ^\circ\text{C})^2 + (0.16\ ^\circ\text{C})^2 + (0.13\ ^\circ\text{C})^2 \\ &\quad \left. + (0.01\ ^\circ\text{C})^2]\right\}^{1/2} = 0.08\ ^\circ\text{C}.\end{aligned}$$

The value of $t(9,0.05)$ is found from Table 15.1 to equal 2.26, so that

$$\varepsilon = \frac{(2.26)(0.08\ ^\circ\text{C})}{\sqrt{10}} = 0.06\ ^\circ\text{C}.$$

Therefore, at the 95% confidence level, $T_{\text{melt}} = 42.70\ ^\circ\text{C} \pm 0.06\ ^\circ\text{C}$.

Exercise 15.16. Assume that the H–O–H bond angles in various crystalline hydrates have been measured to be 108°, 109°, 110°, 103°, 111°, and 107°. Give your estimate of the correct bond angle and its 95% confidence interval.

Rejection of Discordant Data

Sometimes a value differs greatly from the other members of a set of measurements (a *discordant value*) . For example, say that we repeated the measurement of the melting temperature of $Ca(NO_3)_2 \cdot 4H_2O$ in the previous example one more time and obtained a value of 39.75 °C. If we include this eleventh data point, we get a sample mean of 42.43 °C and a sample standard deviation of 0.89 °C. Using the table of Student's t values, we obtain a value for ε of 0.60 °C at the 95% confidence level. Some people think that the only honest thing to do is to report the melting temperature as 42.4 ± 0.6° C. If we assume that our sample standard deviation of 0.89 °C is a good estimate of the population standard deviation, our data point of 39.75 °C is 3.01 standard deviations away from the mean. From the table of the error function in Appendix G, the probability of a randomly chosen member of a population differing from the mean by this much or more is 0.003, or 0.3%. There is considerable justification for asserting that such an improbable event was likely due not to random

[6] William Sealy Gossett, 1876–1937, English chemist and statistician who published under the pseudonym "Student" in order to keep the competitors of his employer, a brewery, from knowing what statistical methods he was applying to quality control.

[7] See Walter Clark Hamilton, *Statistics in Physical Science*, pp. 78ff, The Ronald Press Company, New York, 1964.

[8] John A. Rice, *Mathematical Statistics and Data Analysis*, Wadsworth & Brooks/Cole, Pacific Grove, CA, 1988.

TABLE 15.1 Some Values of Student's t Factor[a]

Number of degrees of freedom ν	Maximum value of Student's t factor for the significance levels indicated			
	$t(\nu,0.60)$	$t(\nu,0.10)$	$t(\nu,0.05)$	$t(\nu,0.01)$
1	1.376	6.314	12.706	63.657
2	1.061	2.920	4.303	9.925
3	0.978	2.353	3.182	5.841
4	0.941	2.132	2.776	4.604
5	0.920	2.015	2.571	4.032
6	0.906	1.943	2.447	3.707
7	0.896	1.895	2.365	3.499
8	0.889	1.860	2.306	3.355
9	0.883	1.833	2.262	3.250
10	0.879	1.812	2.228	3.169
11	0.876	1.796	2.201	3.106
12	0.873	1.782	2.179	3.055
13	0.870	1.771	2.160	3.012
14	0.868	1.761	2.145	2.977
15	0.866	1.753	2.131	2.947
16	0.865	1.746	2.120	2.921
17	0.863	1.740	2.110	2.898
18	0.862	1.734	2.101	2.878
19	0.861	1.729	2.093	2.861
20	0.860	1.725	2.086	2.845
21	0.859	1.721	2.080	2.831
22	0.858	1.717	2.074	2.819
23	0.858	1.714	2.069	2.807
24	0.857	1.711	2.064	2.797
25	0.856	1.708	2.060	2.787
26	0.856	1.706	2.056	2.479
27	0.855	1.703	2.052	2.771
28	0.855	1.701	2.048	2.763
29	0.854	1.699	2.045	2.756
30	0.854	1.697	2.042	2.750
40	0.851	1.684	2.021	2.704
60	0.848	1.671	2.000	2.660
∞	0.842	1.645	1.960	2.576

[a] *John A. Rice, Mathematical Statistics and Data Analysis, Wadsworth & Brooks/Cole, Pacific Grove, CA, 1988, p. 560.*

experimental errors but to some kind of a mistake such as misreading a thermometer or writing down the wrong value. If you assume this, you discard the suspect data point and recompute the mean and standard deviation just as though the discordant data point had not existed. Do not discard more than one data point from a set of data.

There are several different rules for deciding whether to discard a discordant data point. Some people discard data

points that are more than 2.7 standard deviations from the mean (this means 2.7 standard deviations calculated with the discordant point left in). This discards points that have less than a 1% chance of having arisen through normal experimental error. Pugh and Winslow[9] suggest that for a sample of N data points, a data point should be discarded if there is less than one chance in $2N$ that the point came from the same population. This rule discards more points than the first rule for a sample of 10 measurements, since it would discard a point lying 1.96 standard deviations from the mean in a sample of 10 measurements. Since you would expect such a point to occur once in 20 times, the probability that it would occur in a sample of 10 measurements by random chance is fairly large.

The *Q test* is regarded by statisticians as a valid rule for discarding a discordant value. The quantity Q is defined as the difference between an "outlying" data point and its nearest neighbor divided by the difference between the highest and the lowest values in the set:

$$Q = \frac{|(\text{outlying value}) - (\text{value nearest the outlying value})|}{(\text{highest value}) - (\text{lowest value})}. \tag{15.68}$$

An outlying data point is discarded if its value of Q exceeds a certain critical value, which depends on the number of members in the sample. Table 15.2 contains the critical value of Q at the 95% confidence level for samples of N members.[10]

Exercise 15.17. Apply the Q test to the 39.75 °C data point appended to the data set of the previous example.

TABLE 15.2 Critical Q Values at the 95% Probability Level

N	3	4	5	6	7	8	9	10	20	30
Q	0.97	0.84	0.72	0.63	0.58	0.53	0.50	0.47	0.36	0.30

PROBLEMS

1. Assume the following discrete probability distribution:

n	0	1	2	3	4	5
p_n	0.00193	0.1832	0.1054	0.3679	0.7788	1.0000
n	6	7	8	9	10	
p_n	0.7788	0.3679	0.1054	0.18	0.00193	

Find the mean and the standard deviation. Find the probability that x lies between $\langle x\rangle - \sigma_x$ and $\langle x\rangle - \sigma_x$.

2. Assume that a certain biased coin has a 51.0% probability of coming up "heads" when thrown.

(a) Find the probability that in 10 throws five "heads" will occur.
(b) Find the probability that in 10 throws seven "heads" will occur.

3. Calculate the mean and the standard deviation of all of the possible cases of ten throws for the biased coin in the previous problem.

4. Consider the uniform probability distribution such that all values of x are equally probable in the range $-5.00 \prec x \prec 5.00$. Find the mean and the standard deviation. Compare these values with those found in the chapter for a uniform probability distribution in the range $0.00 \prec x \prec 10.00$.

5. Assume that a random variable, x, is governed by the probability distribution

$$f(x) = \frac{c}{x},$$

where x ranges from 1.00 to 10.00.

(a) Find the mean value of x and its variance and standard deviation.
(b) Find the probability that x lies between $\langle x\rangle - \sigma_x$ and $\langle x\rangle - \sigma_x$.

6. Assume that a random variable, x, is governed by the probability distribution (a version of the Lorentzian function)

$$f(x) = \frac{c}{x^2 + 1},$$

where x ranges from -6.000 to 6.000.

(a) Find the mean value of x and its variance and standard deviation.
(b) Find the probability that x lies between $\langle x\rangle - \sigma_x$ and $\langle x\rangle + \sigma_x$.

7. Assume that a random variable, x, is governed by the probability distribution (a version of the Lorentzian function)

$$f(x) = \frac{c}{x^2 + 4},$$

where x ranges from -10.000 to 10.000.

(a) Find the mean value of x and its variance and standard deviation.
(b) Find the probability that x lies between $\langle x\rangle - \sigma_x$ and $\langle x\rangle + \sigma_x$.

8. Find the probability that x lies between $\mu - 1.500\sigma$ and $\mu + 1.500\sigma$ for a Gaussian distribution.

[9] E.M. Pugh and G.H. Winslow, *The Analysis of Physical Measurements*, Addison–Wesley, Reading, MA, 1966.
[10] W.J. Dixon, *Ann. Math. Statist.* **22**, 68 (1951); and R.B. Dean and W.J. Dixon, *Anal. Chem.* **23**, 636 (1951).

9. The *n*th *moment of a probability distribution* is defined by

$$M_n = \int (x - \mu)^n f(x) \mathrm{d}x.$$

The second moment is the variance, or square of the standard deviation. Show that for the Gaussian distribution, $M_3 = 0$, and find the value of M_4 , the fourth moment. Find the value of the fourth root of M_4.

10. Find the third and fourth moments (defined in the previous problem) for the uniform probability distribution such that all values of x in the range $-5.00 \prec x \prec 5.00$ are equally probable. Find the value of the fourth root of M_4.

11. A sample of 10 sheets of paper has been selected randomly from a ream (500 sheets) of paper. The width and length of each sheet of the sample were measured, with the following results:

Sheet number	Width (in.)	Length (in.)
1	8.50	11.03
2	8.48	10.99
3	8.51	10.98
4	8.49	11.00
5	8.50	11.01
6	8.48	11.02
7	8.52	10.98
8	8.47	11.04
9	8.53	10.97
10	8.51	11.00

(a) Calculate the sample mean width and its sample standard deviation, and the sample mean length and its sample standard deviation.

(b) Give the expected error in the width and length at the 95% confidence level.

(c) Calculate the expected ream mean area from the width and length.

(d) Calculate the area of each sheet in the sample. Calculate from these areas the sample mean area and the standard deviation in the area.

(e) Give the expected error in the area from the results of part d.

12. A certain harmonic oscillator has a position given by

$$z = (0.150 \text{ m})[\sin(\omega t)],$$

where

$$\omega = \sqrt{\frac{k}{m}}.$$

The value of the force constant k is 0.455 N m^{-1} and the mass of the oscillator m is 0.544 kg. Find time average of the potential energy of the oscillator over 1.00 period of the oscillator. How does the time average compare with the maximum value of the potential energy?

13. A certain harmonic oscillator has a position given as a function of time by

$$z = (0.150 \text{ m})[\sin(\omega t)],$$

where

$$\omega = \sqrt{\frac{k}{m}}.$$

The value of the force constant k is 0.455 N m^{-1} and the mass of the oscillator m is 0.544 kg. Find time average of the kinetic energy of the oscillator over 1.00 period of the oscillator. How does the time average compare with the maximum value of the kinetic energy?

14. The following measurements of a given variable have been obtained: 23.2, 24.5, 23.8, 23.2, 23.9, 23.5, 24.0. Apply the Q test to see if one of the data points can be disregarded. Calculate the mean of these values, excluding the suspect data point if you decide one can be disregarded.

15. The following measurements of a given variable have been obtained: 68.25, 68.36, 68.12, 68.40, 69.70, 68.53, 68.18, 68.32. Apply the Q test to see if one of the data points can be disregarded. Calculate the mean of these values, excluding the suspect data point if you decide one can be disregarded.

Chapter 16

Data Reduction and the Propagation of Errors

Principal Facts and Ideas

- One type of data reduction is the calculation of some quantity from other measured quantities by the use of a formula.
- Errors in the original measurement propagate through the calculation and can be estimated.
- Another type of data reduction involves fitting a set of data to a formula. This can be done numerically by use of the least-squares (regression) procedure.
- Errors on the curve fitting can be estimated.

Objectives

- Carry out data reduction using mathematical formulas and do an error propagation calculation to determine the probable error in the calculated quantity.
- Carry out data reduction numerically using least-squares methods and determine probable errors in quantities obtained by these methods.

16.1 THE COMBINATION OF ERRORS

Data reduction is the computation of some quantity from measured quantities. An experimental error in a measured quantity will affect the accuracy of any quantity that is calculated from it. This is called *propagation of errors*. The simplest example of data reduction is the adding of two measured quantities. Assume that we require the sum of two quantities, $c = a + b$, and that we have a mean values and 95% confidence intervals for a and b:

$$a = \langle a \rangle \pm \varepsilon_a, \tag{16.1a}$$

$$b = \langle b \rangle \pm \varepsilon_b. \tag{16.2}$$

The probable value of c is

$$\langle c \rangle = \langle a \rangle + \langle b \rangle. \tag{16.3}$$

If we assume that the errors in the two quantities simply add together we get an overestimate, since there is some chance that errors in a and in b will be in opposite directions. If a and b are both governed by Gaussian distributions, mathematicians have shown that c is also governed by a Gaussian distribution, and that the probable error in c is given by

$$\boxed{\varepsilon_c = (\varepsilon_a^2 + \varepsilon_b^2)^{1/2}}. \tag{16.4}$$

Example 16.1. Two lengths have been measured as 24.8 m $\pm$ 0.4 m and 13.6 m $\pm$ 0.3 m. Find the probable value of their sum and its probable error.

The probable value of the sum is 24.8 m + 13.6 m = 38.4 m, and the probable error is

$$\varepsilon = [(0.4 \text{ m})^2 + (0.3 \text{ m})^2]^{1/2} = 0.5 \text{ m}.$$

We report the sum as 38.4 m $\pm$ 0.5 m.

Exercise 16.1. Two time intervals have been clocked as $t_1 = 6.57$ s $\pm$ 0.13 s and $t_2 = 75.12$ s $\pm$ 0.17 s. Find the probable value of their sum and its probable error.

16.1.1 The Combination of Random and Systematic Errors

Random and systematic errors combine in the same way as the errors in Eq. (16.4). If ε_r is the probable error due to

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random errors and ε_s is the probable error due to systematic errors, the total probable error is given by

$$\boxed{\varepsilon_t = (\varepsilon_s^2 + \varepsilon_r^2)^{1/2}}. \tag{16.5}$$

If you use the 95% confidence level for the random errors, you must use the same confidence level for systematic errors if you make an educated guess at the systematic error. Most people instinctively tend to estimate errors at about the 50% confidence level. To avoid this tendency, you might make a first guess at your systematic error and then double it.

Example 16.2. Assume that a length has been measured as 37.8 cm with an expected random error of 0.35 cm and a systematic error of 0.06 cm. Find the total expected error

$$\varepsilon_t = \left[(0.35\text{ cm})^2 + (0.06\text{ cm})^2\right]^{1/2} = 0.36\text{ cm} \approx 0.4\text{ cm},$$
$$l = 37.8\text{ cm} \pm 0.4\text{ cm}.$$

If one source of error is much larger than the other, the smaller error makes a much smaller contribution after the errors are squared. In the previous example, the systematic error is nearly negligible, especially since one significant digit is usually sufficient in an expected error.

Exercise 16.2. Assume that you estimate the total systematic error in a melting temperature measurement as 0.20 °C at the 95% confidence level and that the random error has been determined to be 0.06 °C at the same confidence level. Find the total expected error.

16.1.2 Error Propagation in Data Reduction with a Formula

Measured values are frequently substituted into a formula to obtain a value of some other quantity. For example, in the Dumas method for determining the molar mass of a volatile liquid,[1] we collect the vapor produced by the liquid in a known volume V at a known temperature T and a known pressure P. We then determine the mass of this sample. We assume that the vapor obeys the ideal gas law and apply the formula

$$M = \frac{wRT}{PV}, \tag{16.6}$$

where M is the molar mass, w is the mass of the sample, and R is the ideal gas constant.

Equation (16.6) is an example of a general formula,

$$y = y(x_1, x_2, x_3, \ldots, x_n). \tag{16.7}$$

[1] Lawrence J. Sacks, *Experimental Chemistry*, pp. 26–29, Macmillan Co., New York, 1971.

where $x_1, x_2, x_3, \ldots, x_n$ represent independent variables and y is a dependent variable. Let us assume that we have a mean value and an expected error for each of the independent variables:

$$x_i = \langle x_i \rangle \pm \varepsilon_i \quad (i = 1,2,\ldots,n). \tag{16.8}$$

We need to calculate the expected error in y from the expected errors in $x_1, x_2, \ldots, x_n$. We take an approach based on the fundamental equation of differential calculus, Eq. (8.12)

$$\mathrm{d}y = \left(\frac{\partial y}{\partial x_1}\right)\mathrm{d}x_1 + \left(\frac{\partial y}{\partial x_2}\right)\mathrm{d}x_2 + \left(\frac{\partial y}{\partial x_3}\right)\mathrm{d}x_3 + \cdots + \left(\frac{\partial y}{\partial x_n}\right)\mathrm{d}x_n = \sum_{i=1}^{n}\left(\frac{\partial y}{\partial x_i}\right)\mathrm{d}x_i. \tag{16.9}$$

This equation provides an infinitesimal change $\mathrm{d}y$ due to arbitrary infinitesimal changes $\mathrm{d}x_1, \mathrm{d}x_2, \mathrm{d}x_3, \ldots, \mathrm{d}x_n$.

If finite changes $\Delta x_1, \Delta x_2, \ldots, \Delta x_n$, are made, we can write as an approximation

$$\Delta y \approx \left(\frac{\partial y}{\partial x_1}\right)\Delta x_1 + \left(\frac{\partial y}{\partial x_2}\right)\Delta x_2 + \cdots + \left(\frac{\partial y}{\partial x_n}\right)\Delta x_n = \sum_{i=1}^{n}\left(\frac{\partial y}{\partial x_i}\right)\Delta x_i. \tag{16.10}$$

Assume that we have estimated errors in $x_1, x_2, \ldots$, but of course do not know the actual errors. If we did have the actual errors, we could use Eq. (16.10) to calculate a known error in y. Since we do have the expected errors, one cautious way to proceed would be to assume that all of the expected errors contribute with the same sign and write:

$$\varepsilon_y \approx \left|\left(\frac{\partial y}{\partial x_1}\right)\varepsilon_1\right| + \left|\left(\frac{\partial y}{\partial x_2}\right)\varepsilon_2\right| + \cdots + \left|\left(\frac{\partial y}{\partial x_n}\right)\varepsilon_n\right| = \sum_{i=1}^{n}\left|\left(\frac{\partial y}{\partial x_i}\right)\varepsilon_i\right| \quad \text{(first estimate)}, \tag{16.11}$$

where ε_y (a positive value) represents the expected error in y and where ε_i is the expected error in x_i. This equation overestimates the error in y because there is some probability that some of the errors will cancel instead of adding. An equation that incorporates the statistical probability of error cancelation is

$$\boxed{\varepsilon_y \approx \left[\left(\frac{\partial y}{\partial x_1}\right)^2\varepsilon_1^2 + \left(\frac{\partial y}{\partial x_2}\right)^2\varepsilon_2^2 + \cdots + \left(\frac{\partial y}{\partial x_n}\right)^2\varepsilon_n^2\right]^{\frac{1}{2}} = \left[\sum_{i=1}^{n}\left(\frac{\partial y}{\partial x_i}\right)^2\varepsilon_i^2\right]^{\frac{1}{2}} \text{ (final formula)}}. \tag{16.12}$$

This equation will be our working equation. Since it is based on an equation for differentials, it is more nearly exact if the expected errors are small.

Example 16.3. Find the expression for the propagation of errors for the Dumas molar mass determination. Apply this expression to the following data for *n*-hexane:

$$\begin{aligned} T &= 373.15 \pm 0.25 \text{ K}, \\ V &= 206.34 \pm 0.15 \text{ ml}, \\ P &= 760 \pm 0.2 \text{ torr}, \\ w &= 0.585 \pm 0.005 \text{ g}, \end{aligned}$$

$$\begin{aligned} M &= \frac{(0.585 \text{ g})(0.082057 \text{ l atm K}^{-1} \text{ mol}^{-1})(373.15 \text{ K})}{(1.000 \text{ atm})(0.20634 \text{ l})} \\ &= 86.81 \text{ g mol}^{-1}, \\ \varepsilon_{\text{M}} &\approx \left[\left(\frac{RT}{PV} \right)^2 \varepsilon_w^2 + \left(\frac{wR}{PV} \right)^2 \varepsilon_T^2 + \left(\frac{wRT}{P^2 V} \right)^2 \varepsilon_P^2 \right. \\ &\quad \left. + \left(\frac{wRT}{PV^2} \right)^2 \varepsilon_V^2 \right]^{\frac{1}{2}}. \end{aligned}$$

When we evaluate the partial derivatives, the result is

$$\begin{aligned} \varepsilon_{\text{M}} &= 0.747 \text{ g mol}^{-1}, \\ M &= 86.8 \pm 0.7 \text{ g mol}^{-1}. \end{aligned}$$

The accepted value is 86.17 g mol^{-1}. Our expected error is larger than our actual error, as it should be 95% of the time.

Exercise 16.3. In the cryoscopic determination of molar mass,[2] the molar mass in kg mol^{-1} is given by

$$M = \frac{wK_{\text{f}}}{W \Delta T_{\text{f}}}(1 - K_{\text{f}} \Delta T_{\text{f}}),$$

where W is the mass of the solvent, w is the mass of the unknown solute, ΔT_{f} is the amount by which the freezing point of the solution is less than that of the pure solvent, and K_{f} and K_{f} are constants characteristic of the solvent. A sample of an unknown substance was dissolved in benzene, for which $K_{\text{f}} = 5.12$ K kg mol^{-1} and $K_{\text{f}} = 0.011$ K^{-1}. For the following data, calculate M and its probable error:

$$\begin{aligned} W &= 13.185 \pm 0.003 \text{ g}, \\ w &= 0.423 \pm 0.002 \text{ g}, \\ \Delta T_{\text{f}} &= 1.263 \pm 0.020 \text{ K}. \end{aligned}$$

16.2 CURVE FITTING

There are a number of functional relationships in physical chemistry that allow fitting data to a formula so that the value of another variable can be deduced from the fit. For example, thermodynamic theory implies that the equilibrium pressure of a two-phase system containing one substance is a function only of the temperature:

$$P = P(T). \tag{16.13}$$

Table 16.1 and Figure 16.1 contain a set of student data for the vapor pressure of ethanol, which is the pressure observed when the liquid and the vapor are at equilibrium. Error estimates are included in the table.

TABLE 16.1 Experimental Vapor Pressures of Pure Ethanol at Various Temperature

t (°C)	T (K)	Vapor pressure (Torr)	Expected error (Torr)
25.00	298.15	55.9	3.0
30.00	303.15	70.0	3.0
35.00	308.15	93.8	4.2
40.00	313.15	117.5	5.5
45.00	318.15	154.1	6.0
50.00	323.15	190.7	7.6
55.00	328.15	241.9	8.0
60.00	333.15	304.15	8.8
65.00	338.15	377.9	9.5

The *Clapeyron equation*[3] for any system of one substance and two phases gives the derivative of the function in Eq. (16.13):

$$\frac{\text{d}P}{\text{d}T} = \frac{\Delta H_{\text{m}}}{T \Delta V_{\text{m}}}, \tag{16.14}$$

where P is the pressure, ΔH_m is the molar enthalpy change of the phase transition, T is the absolute temperature, and ΔV_{m} is the molar volume change of the phase transition. If ΔV_{m} is known and the value of the derivative $\text{d}P/\text{d}T$ can be evaluated, then the enthalpy change of vaporization can be calculated. One might draw a tangent line by hand in a graph such as Figure 16.1 and then determine its slope by constructing a right triangle and measuring the rise and run.

Instead of trying to evaluate the derivative, we can proceed by fitting a curve to the data. We first need to integrate the Clapeyron equation to obtain a formula for the curve, and we do this with the following approximations: We assume that the molar volume of the liquid is negligible

[2] Carl W. Garland, Joseph W. Nibler, and David P. Shoemaker, *Experiments in Physical Chemistry*, 7th ed., p. 182, McGraw-Hill, New York, 2003.

[3] The equation is named for Benoît Paul Émile Clapeyron (1799–1864), who was a French engineer and physicist who was one of the founders of thermodynamics.

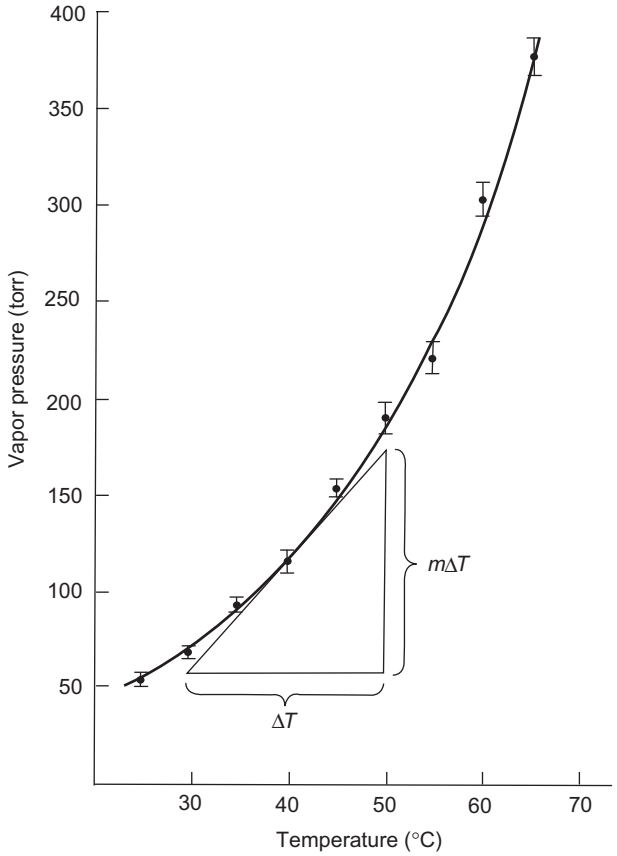

FIGURE 16.1 Experimental vapor pressures of pure ethanol at various temperatures.

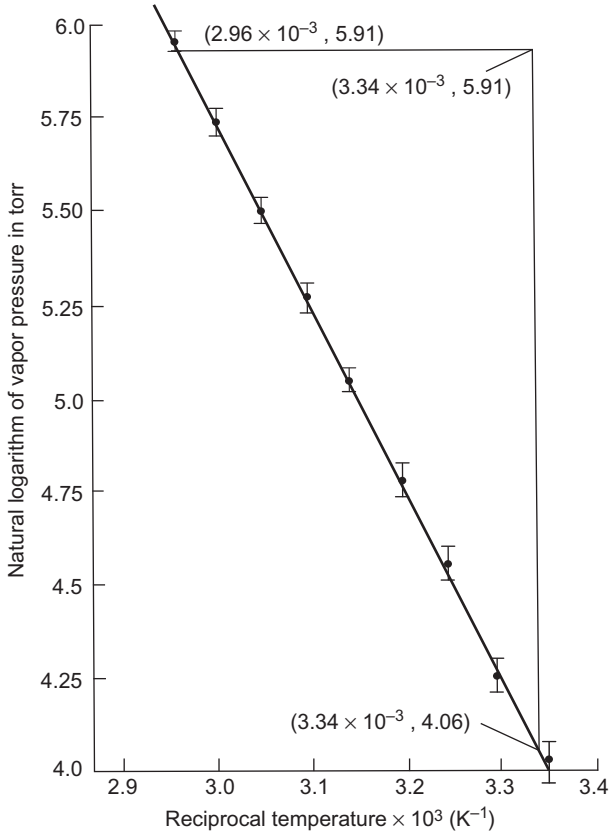

FIGURE 16.2 The natural logarithm of the vapor pressure of ethanol as a function of the reciprocal of the absolute temperature.

compared to that of the gas. This is a good approximation since the molar volume of a vapor is typically several hundred or a thousand times as large as the molar volume of the liquid. We also assume that the vapor is an ideal gas and assume that $\mathbf{\Delta} H_{\mathrm{m}}$ is independent of the temperature. These are also good approximations. We now have

$$\begin{aligned} \Delta V_{\mathrm{m}} &= V_{\mathrm{m}}(\mathrm{gas}) - V_{\mathrm{m}}(\mathrm{liquid}) \approx V_{\mathrm{m}}(\mathrm{gas}) \\ &\approx \frac{RT}{P}, \end{aligned} \tag{16.15}$$

so that

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{P\mathbf{\Delta} H_{\mathrm{m}}}{RT^2}. \tag{16.16}$$

Dividing by P and carrying out an indefinite integration, we obtain the *Clausius-Clapeyron equation*:

$$\ln(P) = -\frac{\mathbf{\Delta} H_{\mathrm{m}}}{RT} + C, \tag{16.17}$$

where C is a constant of integration. Equation (16.17) is a linear relation between $\ln(P)$ and $1/T$. We say that we have *linearized* the data. Figure 16.2 shows $\ln(P)$ as a function of $1/T$. If we can fit a straight line to these data, we can determine the value of the enthalpy change of vaporization.

16.2.1 The Method of Least Squares (Regression)

The method of least squares is a numerical procedure for finding a continuous function that best fits a set of data points, represented by ordered pairs of numbers, $(x_1, y_1), (x_2, y_2), (x_3, y_3)$, etc., where x is the independent variable and y is the dependent variable. We assume that there is some function

$$y = y(x) \tag{16.18}$$

governing y as a function of x, and that we know a family of functions to which the correct function belongs,

$$y = f(x, a_1, a_2, \ldots, a_p). \tag{16.19}$$

In this expression the a's are parameters (constants that have different values for different members of the family). We want to find the values of the parameters that specify the member of the assumed family that most nearly fits the data points.

We define the *residual* for the ith data point as the difference between the measured value and the value of

the optimal function at that point:

$$r_i = y_i - f(x_i, a_1, a_2, \ldots, a_p). \tag{16.20}$$

When a function has been chosen that fits the points well, these residuals will collectively be small. Mathematicians have shown that under certain conditions that the best fit is obtained when the sum of the squares of the residuals is minimized. The method of finding the best curve to fit a set of data points by minimizing this sum is called the *method of least squares*. The method is also called *regression*. It was first applied by Galton.[4] He studied the sizes of plants and their offspring and the heights of fathers and sons. He found in these cases that there was a correlation between the trait in the second generation and the earlier generation. He also found that the offspring tended to be closer to the mean of the trait than the earlier generation. He called this tendency "regression toward mediocrity" and it has also been called "regression toward the mean." The name "regression" has stuck to the method, in spite of the fact that the original meaning of this word does not describe the concept of the method.

We seek the minimum of S_r, the sum of the squares of the residuals,

$$S_r = \sum_{i=1}^{N} \left[y_i - f(x_i, a, a_2, \ldots, a_p) \right]^2, \tag{16.21}$$

where N is the number of data points. This minimum occurs where all of the partial derivatives of S_r with respect to $a_1, a_2, \ldots, a_p$ vanish:

$$\frac{\partial S_r}{\partial a_i} = 0 \quad (i = 1, 2, \ldots, p). \tag{16.22}$$

This is a set of simultaneous equations, one for each parameter. For some families of functions, these simultaneous equations are nonlinear equations and are solved by successive approximations.[5] For linear functions or polynomial functions, the equations are linear equations, and we can solve them by the methods of Chapter 14.

16.2.2 Linear Least Squares (Linear Regression)

In the method of *linear least squares* or *linear regression*, we seek the linear function that minimizes the sum of the squares of the residuals. This applies to the Clausius-Clapeyron equation since ln (P) is a linear function of $1/T$. The family of *linear functions* is given by

$$y = mx + b. \tag{16.23}$$

[4] Sir Francis Galton (1822–1911) was a famous British eneticist.

[5] Garland, Nibler, and Shoemaker, *op. cit.*, pp. 724 ff.

The sum of the squares of the residuals is

$$S_r = \sum_{i=1}^{N} (y_i - mx_i - b)^2. \tag{16.24}$$

We seek that value of the slope m and that value of the intercept b that minimize the value of R. As in Chapter 8, we differentiate with respect to m and b and set the derivatives equal to zero. The simultaneous equations are

$$\begin{aligned} \frac{\partial S_r}{\partial m} &= 2 \sum_{i=1}^{N} (y_i - mx_i - b)(-x_i) \\ &= 2 \sum_{i=1}^{N} (-x_i y_i + mx_i^2 + bx_i) = 0, \end{aligned} \tag{16.25}$$

$$\begin{aligned} \frac{\partial S_r}{\partial b} &= 2 \sum_{i=1}^{N} (y_i - mx_i - b)(-1) \\ &= 2 \sum_{i=1}^{N} (-y_i + mx_i + b) = 0. \end{aligned} \tag{16.26}$$

This is a set of linear inhomogeneous simultaneous equations in m and b. We divide by 2 and write them in the form

$$S_{x^2} m + S_x b = S_{xy}, \tag{16.27}$$

$$S_x m + Nb = S_y, \tag{16.28}$$

where

$$S_x = \sum_{i=1}^{N} x_i, \tag{16.29}$$

$$S_y = \sum_{i=1}^{N} y_i, \tag{16.30}$$

$$S_{xy} = \sum_{i=1}^{N} x_i y_i, \tag{16.31}$$

$$S_{x^2} = \sum_{i=1}^{N} x_i^2. \tag{16.32}$$

From *Cramer's rule* in Chapter 14

$$\boxed{m = \frac{\begin{vmatrix} S_{xy} & S_x \\ S_y & N \end{vmatrix}}{\begin{vmatrix} S_{x^2} & S_x \\ S_x & N \end{vmatrix}} = \frac{NS_{xy} - S_x S_y}{NS_{x^2} - S_x^2} = \frac{NS_{xy} - S_x S_y}{D}}, \tag{16.33}$$

$$\boxed{b = \frac{\begin{vmatrix} S_{x^2} & S_{xy} \\ S_x & S_y \end{vmatrix}}{\begin{vmatrix} S_{x^2} & S_x \\ S_x & N \end{vmatrix}} = \frac{S_{x^2}S_y - S_x S_{xy}}{NS_{x^2} - S_x^2} = \frac{S_{x^2}S_y - S_x S_{xy}}{D}}, \tag{16.34}$$

where

$$\boxed{D = NS_{x^2} - S_x^2}. \tag{16.35}$$

These are our working equations. The calculation of the four sums can be carried out by hand if there are not too many data points, but many calculators and computer programs carry out the calculation automatically.

Example 16.4. Calculate the slope m and the intercept b for the least-squares line for the data in Table 16.1, using $\ln(P)$ as the dependent variable and $1/T$ as the independent variable. Calculate the enthalpy change of vaporization from the slope.

When the numerical work is done, the results are

$$\begin{aligned} m &= -4854 \text{ K}, \\ b &= 20.28, \\ \Delta H_{\text{m}} &= -mR = (-4854 \text{ K})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= 40.36 \times 10^3 \text{ J mol}^{-1} = 40.36 \text{ kJ mol}^{-1}. \end{aligned}$$

This value compares with the accepted value of 40.3 kJ mol^{-1}.

Exercise 16.4. The following data give the vapor pressure of water at various temperatures.[6] Transform the data, using $\ln(P)$ for the dependent variable and $1/T$ for the independent variable. Carry out the linear least-squares fit by hand, calculating the four sums. Find the molar enthalpy change of vaporization.

Temperature (°C)	Vapor pressure (Torr)
0	4.579
5	6.543
10	9.209
15	12.788
20	17.535
25	23.756

[6] R. Weast, Ed., *Handbook of Chemistry and Physics*, 51st ed., p. D-143, CRC Press, Boca Raton, FL, 1971–1972.

Sometimes it is necessary to try two or more families of functions to determine which gives the best fit. If it is possible to transform different possible formulas into linear form, we can use linear least-squares to test the possibilities. Nonlinear least-squares procedures can also be carried out. If there is no back reaction, the concentration of a single reactant undergoing a first-order chemical reaction is given by.

$$c = c_0 e^{-kt}, \tag{16.36}$$

where c_0 is the initial concentration and k is the rate constant. This can be linearized by taking the logarithm of both sides of the equation:

$$\ln(c) = \ln(c_0) = kt. \tag{16.37}$$

If there is no back reaction and if the reaction is a second order, the concentration of the reactant is given by

$$\frac{1}{c} = kt + \frac{1}{c_0}, \tag{16.38}$$

where k is the rate constant and C is a constant of integration. This is a linear relation if we use $1/c$ as the dependent variable. If there is no back reaction and the reaction is third order, the concentration c of the reactant is given by

$$\frac{1}{2c^2} = kt + \frac{1}{2c_0^2}. \tag{16.39}$$

This is linear relation if we use $1/2c^2$ or $1/c^2$ as the dependent variable. To determine the order of a reaction, we can try three different linear least-squares fits: one using $\ln(c)$ as the dependent variable, one using $1/c$ as the dependent variable, and one using $1/c^2$ as the dependent variable. We then determine which one most nearly fits the data.

Once the least-squares line has been found, the residuals can be calculated from

$$r_i = y_i - mx_i - b. \tag{16.40}$$

We can evaluate a fit by examining the residuals. The sum of the residuals is always equal to zero in a least-squares fit, and in a good fit the residuals will be either positive or negative without any pattern. For a poor fit, there can be a general curvature in the graph and the residuals will have the same sign near the ends of the graph and the other sign in the middle.

Example 16.5. The following is a fictitious set of data for the concentration of the reactant in a chemical reaction with one reactant and negligible back reaction. Determine whether the reaction is first, second, or third order. Find the rate constant and the initial concentration.

Time (min)	Concentration (mol l^{-1})
5.0	0.715
10.0	0.602
15.0	0.501
20.0	0.419
25.0	0.360
30.0	0.300
35.0	0.249
40.0	0.214
45.0	0.173

We test for first order by attempting a linear fit using $\ln(c)$ as the dependent variable and t as the independent variable. The result is

$$\begin{aligned} m &= -0.03504 \text{ min}^{-1} = -k, \\ b &= -0.1592 = \ln[c(0)], \\ c(0) &= 0.853 \text{ mol l}^{-1}. \end{aligned}$$

The following set of residuals was obtained:

$$\begin{aligned} r_1 &= -0.00109, & r_6 &= 0.00634, \\ r_2 &= 0.00207, & r_7 &= -0.00480, \\ r_3 &= -0.00639, & r_8 &= 0.01891, \\ r_4 &= -0.00994, & r_9 &= -0.01859. \\ r_5 &= 0.01348, \end{aligned}$$

This is a good fit, with no pattern of general curvature shown in the residuals. We test the hypothesis that the reaction is second order by attempting a linear fit using $1/c$ as the dependent variable and t as the independent variable. The result is

$$\begin{aligned} m &= 0.1052 \text{ l mol}^{-1} = k, \\ b &= 0.4846 \text{ l mol}^{-1} = \frac{1}{c(0)}, \\ c(0) &= 2.064 \text{ mol l}^{-1}. \end{aligned}$$

The following set of residuals was obtained:

$$\begin{aligned} r_1 &= 0.3882, & r_6 &= -0.3062, \\ r_2 &= 0.1249, & r_7 &= -0.1492, \\ r_3 &= -0.0660, & r_8 &= -0.0182, \\ r_4 &= -0.2012, & r_9 &= 0.5634, \\ r_5 &= -0.3359. \end{aligned}$$

This is not such a satisfactory fit as in the first-order fit, since the residuals show a general curvature, beginning with positive values, becoming negative, and then becoming positive again. We now test the hypothesis that the reaction is third order by attempting a linear fit using $1/(2c^2)$ as the dependent variable and t as the independent variable. The results are

$$\begin{aligned} m &= 0.3546 \text{ l}^2 \text{ mol}^{-2} \text{ min}^{-1} = k, \\ b &= -3.054 \text{ l}^2 \text{ mol}^{-2}. \end{aligned}$$

This is obviously a bad fit, since the intercept b should not be negative. The residuals are

$$\begin{aligned} r_1 &= 2.2589, & r_6 &= -2.0285, \\ r_2 &= 0.8876, & r_5 &= -1.2927, \\ r_3 &= -0.2631, & r_8 &= -0.2121, \\ r_4 &= -1.1901, & r_9 &= 3.8031. \\ r_5 &= -1.9531, \end{aligned}$$

Again, there is considerable curvature. The reaction is apparently first order, with the rate constant and initial concentration given in the first fit.

16.2.3 The Correlation Coefficient and the Covariance

The *correlation coefficient* is an objective measure of the closeness of a least-squares fit. For linear least squares, the correlation coefficient is defined by

$$\boxed{r = \frac{NS_{xy} - S_x S_y}{[(NS_{x^2} - S_x^2)(NS_{y^2} - S_y^2)]^{1/2}}} \quad \text{(definition)}, \qquad (16.41)$$

where S_x, S_y, S_{xy}, and S_{x^2} have been defined and where

$$S_{y^2} = \sum_{i=1}^{N} y_i^2. \qquad (16.42)$$

If the data points lie exactly on the least-squares line, the correlation coefficient will be equal to 1 if the slope is positive or to -1 if the slope is negative. The square of the correlation coefficient is ordinarily reported. If the data points are scattered randomly about the graph so that no least-squares line can be found, the correlation coefficient will equal zero. In a fairly close fit, the square of the correlation coefficient might equal 0.98 or 0.99.

Example 16.6. Calculate the correlation coefficients for the three linear fits in the previous example.

Use of Eq. (16.41) gives the results:

For the first-order fit, $r = -0.9997$.
For the second-order fit, $r = 0.9779$.
For the third-order fit, $r = 0.9257$.

The first-order fit is the best.

The correlation coefficient is related to a quantity called the *covariance*, defined by[7]

$$s_{x,y} = \frac{1}{N-1}\sum_{i-1}^{N}(x_i - \langle x\rangle)(y_i - \langle y\rangle) \quad \text{(definition)}, \tag{16.43}$$

where $\langle x\rangle$ is the mean value of the xs,

$$\langle x\rangle = \frac{1}{N}S_x, \tag{16.44}$$

and where $\langle y\rangle$ is the mean value of the ys,

$$\langle y\rangle = \frac{1}{N}S_y. \tag{16.45}$$

The covariance has the same general behavior as the correlation coefficient. A larger magnitude indicates a closer fit. If large values of x tend to occur with small values of y, the covariance will be negative, and if large values of x tend to occur with large values of y, the covariance will be positive. If there is no relationship between x and y, the covariance will equal zero

Example 16.7. Calculate the covariance for the following ordered pairs:

y	x
−1.00	0.00
0	1.00
1.00	2.00
2.00	3.00
3.00	4.00

$$\begin{aligned}\langle x\rangle &= 2.00,\\ \langle y\rangle &= 1.00,\\ s_{x,y} &= \frac{1}{4}(4.00 + 1.00 + 0.00 + 1.00 + 4.00)\\ &= \frac{10.00}{4} = 2.500.\end{aligned}$$

These pairs correspond to a linear fit with correlation coefficient squared equal to 1.000.

Exercise 16.5. Calculate the covariance for the following ordered pairs:

y	x
−1.00	0.00
0	1.00
1.00	0.00
0.00	−1.00

16.2.4 Error Propagation in Linear Least Squares

Our task is to find the probable errors in the slope and intercept of a least-squares line. We consider two cases:

1. The expected errors in the values of the dependent variable are known.
2. The expected errors in the values of the dependent variable are not known.

In both cases, we assume that the errors in the values of the independent variable x are negligible.

Case 1. Let the expected error in the value of y_i be denoted by ε_i. Equations for the slope and the intercept of the least-squares line are given in Eqs. (16.33) and (16.34). The ys play the role of independent variables in these equations, so we can apply Eq. (16.12). The expected error in the slope is given by

$$\begin{aligned}\varepsilon_{\mathrm{m}} &= \left[\frac{1}{D}\sum_{i=1}^{N}\left(\frac{\partial m}{\partial y_i}\right)^2\varepsilon_i^2\right]^{1/2}\\ &= \left[\frac{1}{D^2}\sum_{i=1}^{N}(Nx_i - S_x)^2\varepsilon_i^2\right]^{1/2},\end{aligned} \tag{16.46}$$

where D and S_x are given in Eqs. (16.29) and (16.35). In the case that all of the expected errors in the y's are all equal to ε_y,

$$\begin{aligned}\varepsilon_{\mathrm{m}} &= \left[\frac{1}{D}\sum_{i=1}^{N}(Nx_i - S_x)^2\right]^{1/2}\varepsilon_y\\ &= \left[\frac{1}{D^2}\sum_{i=1}^{N}(N^2x_i^2 - 2Nx_iS_x + S_x^2)^2\right]^{1/2}\varepsilon_y\\ &= \left[\frac{1}{D^2}\left(N^2S_{x^2} - 2NS_x^2 + NS_x^2\right)\right]^{1/2}\varepsilon_y\\ &= \left[\frac{1}{D^2}\left(N^2S_{x^2} - NS_x^2\right)\right]^{1/2}\varepsilon_y\\ &= \left[\frac{1}{D^2}(ND)\right]^{1/2}\varepsilon_y = \left(\frac{N}{D}\right)^{1/2}\varepsilon_y.\end{aligned} \tag{16.47}$$

[7] John E. Freund, *Modern Elementary Statistics*, 7th ed., p. 459, Prentice–Hall, Englewood Cliffs, NJ, 1988.

The intercept is given by

$$b = \frac{S_{x^2} S_y - S_x S_{xy}}{D}, \tag{16.48}$$

so that

$$\frac{\partial b}{\partial y_i} = \frac{S_{x^2} - S_x x_i}{D}, \tag{16.49}$$

where we use the facts

$$\frac{\partial S_y}{\partial y_i} = 1,$$

$$\frac{\partial S_{xy}}{\partial y_i} = x_i,$$

$$\varepsilon_b = \left[\sum_{i=1}^{N} \left(\frac{\partial b}{\partial y_i}\right)^2 \varepsilon_i^2\right]^{1/2}$$

$$= \left[\frac{1}{D^2} \sum_{i=1}^{N} (S_{x^2} - S_x x_i)^2 \varepsilon_i^2\right]^{1/2}, \tag{16.50}$$

where S_{x^2} is given by Eq. (16.32). For the case that all of the ε_is are all equal to ε_y

$$\varepsilon_b = \left[\frac{1}{D^2} \sum_{i=1}^{N} (S_{x^2} - S_x x_i)^2\right]^{1/2} \varepsilon_y$$

$$= \left[\frac{1}{D^2} \sum_{i=1}^{N} (S_{x^2}^2 - 2S_{x^2} S_x x_i + S_x^2 x_i^2)\right]^{1/2} \varepsilon_y$$

$$= \left[\frac{1}{D^2} \left(N S_{x^2}^2 - 2S_{x^2} S_x^2 + S_x^2 S_{x^2}\right)\right]^{1/2} \varepsilon_y$$

$$= \left[\frac{1}{D^2} \left(N S_{x^2}^2 - S_{x^2} S_x^2\right)\right]^{1/2} \varepsilon_y$$

$$= \left[\frac{D}{D^2} \left(S_{x^2}\right)\right]^{1/2} \varepsilon_y,$$

$$\boxed{\varepsilon_b = \left(\frac{S_{x^2}}{D}\right)^{1/2} \varepsilon_y}. \tag{16.51}$$

Example 16.8. Assume that the expected error in the logarithm of each vapor pressure in Table 16.1 is equal to 0.040. Find the expected error in the least-squares slope and in the enthalpy change of vaporization.

From the data,

$$D = 1.327 \times 10^{-6}\ \text{K}^{-2},$$

so that

$$\varepsilon_m = \left(\frac{9}{1.327 \times 10^{-6}\ \text{K}^{-2}}\right)^{1/2} (0.040) = 104\ \text{K},$$

$$\varepsilon_{\triangle H_m} = R\varepsilon_m = 870\ \text{J mol}^{-1} = 0.87\ \text{kJ mol}^{-1}$$

$$\approx 0.9\ \text{kJ mol}^{-1},$$

$$\mathbf{\Delta} H_m = 44.6 \times 10^3\ \text{J mol}^{-1} \pm 900\ \text{J mol}^{-1}$$

$$= 44.6\ \text{kJ mol}^{-1} \pm 0.9\ \text{kJ mol}^{-1}.$$

Exercise 16.6. Assume that the expected error in the logarithm of each concentration in Example 16.5 is equal to 0.010. Find the expected error in the rate constant, assuming the reaction to be first order.

Case 2. If we do not have information about the expected errors in the dependent variable, we assume that the residuals are a sample from the population of experimental errors. The variance of the N residuals is given by

$$s_r^2 = \frac{1}{N-2} \sum_{i=1}^{N} r_i^2. \tag{16.52}$$

The standard deviation of the residuals is the square root of the variance:

$$s_r = \left(\frac{1}{N-2} \sum_{i=1}^{N} r_i^2\right)^{1/2}. \tag{16.53}$$

The number of degrees of freedom is $N-2$ because we have calculated two quantities, a least-squares slope and a least-squares intercept from the set of numbers, "consuming" two of the N independent pieces of information. The mean of the residuals does not enter in the formula, because the mean of the residuals in a least-squares fit always vanishes.

Exercise 16.7. Sum the residuals in Example 16.5 and show that this sum vanishes in each of the three least-square fits.

Equation (16.53) provides an estimate of the standard deviation of the population of experimental errors. We assume that the errors in y are distributed according to the Student t distribution, so the expected error in y at the 95% confidence level is given by

$$\boxed{\varepsilon_y = t(\nu, 0.05) s_r} \tag{16.54}$$

where $t(v, 0.05)$ is the Student t factor for $\nu = N-2$; the number of degrees of freedom and where s_r is the standard deviation of the residuals.

We can now write expressions similar to Eqs. (16.47) and (16.50) for the expected errors at the 95% confidence level:

$$\varepsilon_m = \left(\frac{N}{D}\right)^{1/2} t(\nu, 0.05) s_r \tag{16.55}$$

and

$$\varepsilon_b = \left(\frac{1}{D} \sum_{i=1}^{N} x_i^2\right)^{1/2} t(\nu, 0.05) s_r. \tag{16.56}$$

The standard deviations of the slope and intercept are given by similar formulas without the Student t factor:

$$s_m = \left(\frac{1}{D} \sum_{i=1}^{N} x_i^2\right)^{1/2} \qquad s_r = \left(\frac{S_{x^2}}{D}\right)^{1/2} s_r, \tag{16.57}$$

$$s_b = \left(\frac{N}{D}\right)^{1/2} s_r. \tag{16.58}$$

Example 16.9. Calculate the residuals for the linear least-squares fit of Example 16.4. Find their standard deviation and the probable error in the slope and in the enthalpy change of vaporization, using the standard deviation of the residuals.

Numbering the data points from the 25 °C point (number 1) to the 65 °C point (number 9), we find the residuals:

$$\begin{aligned} r_1 &= 0.0208, & r_6 &= -0.0116, \\ r_2 &= -0.0228, & r_7 &= -0.0027, \\ r_3 &= 0.0100, & r_8 &= 0.0054, \\ r_4 &= -0.0162, & r_9 &= 0.0059. \\ r_5 &= 0.0113, \end{aligned}$$

The standard deviation of the residuals is

$$s_r = 0.0154.$$

Using the value of D from the previous example, the uncertainty in the slope is

$$\begin{aligned} \varepsilon_{\mathrm{m}} &= \left(\frac{9}{1.327 \times 10^{-6}\ \mathrm{K}^{-2}}\right)^{1/2} (2.365)(0.0154) \\ &= 94.9\ \mathrm{K}, \end{aligned}$$

where we have used the value of the Student's t factor for seven degrees of freedom from Table 15.1. The uncertainty in the enthalpy change of vaporization is

$$\begin{aligned} \varepsilon_{\Delta H_{\mathrm{m}}} &= R\varepsilon_{\mathrm{m}} = (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(96.9\ \mathrm{K}) \\ &= 789\ \mathrm{J\ mol^{-1}}. \end{aligned}$$

Exercise 16.8. Assuming that the reaction in Example 16.5 is first order, find the expected error in the rate constant, using the residuals as estimates of the errors.

16.2.5 Carrying Out Least-Squares Fits with Excel

The following instructions are written for Excel 2010 for Windows. If you have a different version of this spreadsheet or if you are using a Macintosh computer, there will be differences in the procedure. The Excel spreadsheet will carry out least-squares fits in two different ways. You can carry out linear least-squares fits in a worksheet, or you can carry out linear and various nonlinear least-squares procedures on a graph. The advantage of the worksheet procedure is that the residuals and the expected errors in the slope and intercept of the linear fit are provided by the software. The advantage of the graph procedure is that nonlinear least-squares fits can be carried out.

Linear Least-Squares Fits in a Worksheet

The Excel 2010 spreadsheet program is usually delivered with some of its functions disabled. In order to carry out linear least-squares fits in a worksheet, the Analysis ToolPak must be enabled. To this, you open a worksheet and select "Options" in the pull-down menu obtained by clicking on the "File" icon. When a window appears, double-click on "Add-ins." At the bottom of the window, you should see the word "Manage" with "Excel Add-Ins" showing. If this is not showing, scroll until it appear and then click on "Go." A list of available Add-Ins appears, Select either "Analysis ToolPak" or "Analysis ToolPak VBA," which includes the Visual Basic programming language. Click on the box adjacent to the name of the Add-In, not on the name itself. You can select more than one Add-In. Then click on "OK." The icon for the Analysis ToolPak should appear at the right end of the toolbar for the "Data" tab, labeled "Data Analysis."

The first step in carrying out linear least-squares fits in a worksheet you open a worksheet and enter the data points into columns of the worksheet. The column for the independent (x) variable does not have to be immediately to the left of the column for the dependent (y) variable as it does in making a graph. If necessary, use formulas to transform your original data into variables that will give a linear fit. Click on the Data tab. Click on the Data Analysis icon at the right end of the Data tab toolbar. A list of tools should appear. Select Regression and click on OK. A window appears with several blanks. In the Input Y Range blank, type in the first and last cell addresses of the dependent variable, separated by a colon (:). If the values are in the first ten rows of column B, you type B1:B10. In the Input X Range blank, type in the cell addresses for the independent variable, such as A1:A10. In the Confidence Level blank, choose 95%. You will probably want to see a list of the residuals, so check the Residuals box. If you want to see a plot of the residuals, check the Residuals Plot box. You can specify where you want to put the output. The output occupies several columns and several rows, so it is best to check the "New Worksheet" box. Otherwise, specify a cell on your worksheet where you want to put the upper left corner of the output area. Click on OK.

When you click on OK, the computer carries out the procedure and puts the output on the screen. A number of statistical parameters are exhibited. The value of the correlation coefficient and its square will be in the R Square cell. At the bottom of the output are columns labeled Coefficient, Standard Error, t Stat, P-Value, Lower 95%, and Upper 95%. There are two rows for the intercept and slope (which is labeled "X variable"). The Coefficient column contains the slope and the intercept. The Standard Error column contains the error based on the standard deviation (about 68% confidence). The Lower 95% column contains

the parameter decremented by the expected error at the 95% confidence level, and the Upper 95% column contains the parameter incremented by the expected error. To obtain the expected error, you will have to do a subtraction. You should look at the list of residuals and the plot of the residuals to see it there is a systematic curvature in the data, which shows up with residuals having one sign at the ends of the fit and the other sign in the middle.

Least-Squares Fits on a Graph

With this option, you can make a variety of fits in addition to a linear fit. To begin a fit, you make a worksheet in the usual way, with the values of the independent variable in one column and the values of the dependent variable in the column just to the right of that column. Select the two columns. Make a graph in the usual way by selecting the "Scatter" option in the "Insert" menu. Choose the option that does not place a curve in the graph. When you have made the graph, click on the "Layout" tab in the "Chart Tools" tab and click on the "Trendline" tab. A menu appears. Click on "More Trendline Options." There are several options, including a linear fit. Click on the one you need. Click on "Display Equation on chart" and click on "Display R-squared value on chart." If you want the displayed curve to extend past your first and last data points, click on Forecast and specify how far on the x axis you want the curve to extend in the forward and back directions. Click on "Close" and the computer carries out the fit. The least-squares curve, the equation of the fitting function, and the square of the correlation coefficient appear on the graph. If you want more digits for the equation parameters or want scientific notation, double-click on the equation. A window appears. Click on "Number." A window appears in which you can choose whether you want scientific notation or ordinary notation and can specify the number of digits after the decimal point.

Exercise 16.9. The following is a set of data for the following reaction at 25 °C.[8]

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr.$$

Using linear least squares, determine whether the reaction obeys first-order, second-order, or third-order kinetics and find the value of the rate constant.

Time/h	$[(CH_3)_3CBr]$/mol l^{-1}
0	0.1051
5	0.0803
10	0.0614
15	0.0470
20	0.0359
25	0.0274
30	0.0210
35	0.0160
40	0.0123

Exercise 16.10. Take the data from the previous exercise and test for first order by carrying out an exponential fit using Excel. Find the value of the rate constant.

16.2.6 Some Warnings About Least-Squares Procedures

It is a poor idea to rely blindly on a numerical method, so you should determine whether your results are reasonable. An unreasonable value usually indicates a problem in the manipulations used to linearize the data or an incorrectly entered data point. You should always look at your correlation coefficient. A low magnitude usually indicates a problem. You should always inspect the graph corresponding to a fit. If there is a bad data point, you will probably be able to spot it. If the data points show a general curvature, you will probably be able to tell that as well from the graph.

A final warning is that in making a change in variables in order to do a linear fit, you are changing the relative importance, or weight, of the various data points.[9] In analyzing reaction rate data, fitting $\ln(c)$ to a straight line $\ln(c) = -kt + C$ will not necessarily give the same value of k as will fitting c to the function $c = e^C e^{-kt}$. We now discuss a way to compensate for this and to compensate for expected errors of different sizes in different data points.

16.2.7 Weighting Factors in Linear Least Squares

This procedure is not supported by the Excel spreadsheet. To implement this procedure, you will probably need to compute the relevant sums yourself. Consider the case that we want to make a linear least-squares fit to a set of data in which not all data points should have equal importance.

[8] L.C. Bateman, E.D. Hughes, and C.K. Ingold, "Mechanism of Substitution at a Saturated Carbon Atom. Part XIX. A Kinetic Demonstration of the Unimolecular Solvolysis of Alkyl Halides," *J. Chem. Soc*. 960 (1940).

[9] Donald E. Sands, "Weighting Factors in Least Squares," *J. Chem. Educ*. **51**, 473 (1974).

We assume that the error in y_i is a member of a population of experimental errors with standard deviation σ_i. Instead of minimizing the sum of the squares of the residuals, mathematicians have shown that we should minimize[10] the sum of the squares of the residuals divided by these standard deviations

$$S'_r = \sum_{i=1}^{N} \frac{r_i^2}{\sigma_i^2} = \sum_{i=1}^{N} \frac{1}{\sigma_i^2}(y_i - mx_i - b)^2, \qquad (16.59)$$

where we denote the sum by the symbol S'_r. The factors $1/\sigma_i^2$ in the sum are called *weighting factors* and give greater importance to data points with smaller expected errors.

We now minimize S'_r. The equations are similar to the equations for ordinary (unweighted) linear least squares, except that the sums include the weighting factors given by $1/\varepsilon_i^2$. The results for the slope and intercept are

$$m = \frac{1}{D'}(S'_1 S'_{xy} - S'_x S'_y), \qquad (16.59a)$$

$$b = \frac{1}{D'}(S'_{x^2} S'_y - S'_x S'_{xy}), \qquad (16.60)$$

where

$$D' = S'_1 S'_{x^2} - S'_x 2 \qquad (16.61a)$$

and where

$$S'_1 = \sum_{i=1}^{N} \frac{1}{\sigma_i^2}, \qquad (16.61b)$$

$$S'_x = \sum_{i=1}^{N} \frac{x_i}{\sigma_i^2}, \qquad (16.62)$$

$$S'_y = \sum_{i=1}^{N} \frac{y_i}{\sigma_i^2}, \qquad (16.63)$$

$$S'_{xy} = \sum_{i=1}^{N} \frac{x_i y_i}{\sigma_i^2}, \qquad (16.64)$$

$$S'_{x^2} = \sum_{i=1}^{N} \frac{x_i^2}{\sigma_i^2}. \qquad (16.65)$$

The standard deviations are generally unknown, so we cannot use them to determine the weighting factors. If we have known expected errors for the different data points, we can replace the standard deviations by the expected errors and minimize the sum

$$S''_r \sum_{i=1}^{N} \frac{r_i^2}{\varepsilon_i^2} = \sum_{i=1}^{N} \frac{1}{\varepsilon_i^2}(y_i - mx_i - b)^2. \qquad (16.66)$$

with similar modifications in the definitions of the S sums.

[10] P.R. Bevington and D.K. Robinson, *Data Reduction and ErrorAnalysis for the Physical Sciences*, 2nd ed., McGraw–Hill, New York, 1992.

If the values of the dependent variable have equal expected errors, an unweighted least-squares fit is appropriate. However, if we linearize by taking a function of the original variable, then the original expected errors will not generally produce equal errors in the new variable, and the weighted least-squares procedure is preferred. For example, if y_i has an expected error ε_i then the error in $\ln(y_i)$ has an expected error given approximately by

$$\varepsilon(\ln(y_i)) \approx \frac{\mathrm{d}\ln(y_i)}{\mathrm{d}y_i}\varepsilon_i = \frac{1}{y_i}\varepsilon_i. \qquad (16.67)$$

Example 16.10. Find the least-squares line for the data of Table 16.1, assuming that the weighting factors are inversely proportional to the squares of the expected errors in the logarithms.

The expected errors in $\ln(P)$ were calculated from the expected errors in the pressures given in the table, using Eq. (16.67). These were substituted into the equations for the sums in place of the σ_is. The results were

$$m = -4872 \text{ K},$$
$$b = 20.34.$$

These values differ slightly from those of Example 16.4, and these values are likely more nearly correct. The enthalpy change of vaporization is

$$\Delta H_\mathrm{m} = -Rm = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(-4872 \text{ J mol}^{-1})$$
$$= 40501 \text{ J mol}^{-1} = 40.51 \text{ kJ mol}^{-1}.$$

In the following exercise, you can see what an inaccurate point can do if the unweighted least-squares procedure is used.

Exercise 16.11. Change the data set of Table 16.1 by adding a value of the vapor pressure at 70 °C of 421 torr ± 40 torr. Find the least-squares line using both the unweighted and weighted procedures.

This discussion suggests a possible procedure to use if you do not know expected errors for your data. First you carry out an unweighted least-squares fit and find the residuals. Carry out the fit a second time using weighting factors, utilizing the residuals from the first fit in place of the σ_is of Eq. (16.59). This procedure should give a better fit than use of the unweighted procedure. If there is only one data point with a residual that is much larger in magnitude than the others, a reasonable procedure would be to calculate the standard deviation of the residuals after an initial fit and to disregard the data point if its residual is at least as large as the standard deviation of the residuals times 2.7, which corresponds to a probability of less than 1% that the data point arose from experimental error. Do not disregard more than one point.

16.2.8 Linear Least Squares with Fixed Slope or Intercept

At times we need to carry out a linear least-squares fit with the constraint that either the slope or the intercept must have a specific value. If the intercept is fixed, one minimizes the sum of the squares of the residuals only with respect to the slope m. This is the same as given in Eq. (16.25):

$$\frac{dR}{dm} = 2\sum_{i=1}^{N}(y_i - mx_i - b)(-x_i) = 0, \tag{16.68}$$

where b is the fixed value of the intercept. The solution to this equation is

$$m = \frac{S_{xy} - bS_x}{S_{x^2}}, \tag{16.69}$$

where the sums have the same definitions as before. If the slope m is required to have a fixed value, we have only the equation for b, which is the same as Eq. (16.26)

$$\frac{dR}{db} = 2\sum_{i=1}^{N}(y_i' - mx_i - b)(-1) = 0. \tag{16.70}$$

The solution to this is

$$b = \frac{S_y - mS_x}{N}. \tag{16.71}$$

If the required slope is equal to zero, the resulting intercept is equal to the mean of the y values

$$b = \frac{S_y}{N} = \langle y \rangle. \tag{16.72}$$

The Excel spreadsheet will carry out fits on a graph with the intercept required to have a specific value. After constructing a graph, select "Trendline" in the "Layout" menu. Then click on the "More Trendline Options" tab and click on the "Set intercept" box and specify 0.00 or another appropriate value for the intercept.

Example 16.11. Using Excel carry out a linear least-squares fit on the following data, once with the intercept fixed at zero and once without specifying the intercept:

x	0	1	2	3	4	5
y	0.05	0.98	2.00	2.99	4.03	4.98

Compare your slopes and your correlation coefficients for the two fits.

With the intercept set equal to zero, the fit is

$$y = 0.9995x,$$
$$r^2 = 0.9998.$$

Without specifying the intercept, the fit is

$$y = 0.994x + 0.02,$$
$$r^2 = 0.9998.$$

Exercise 16.12. Carry out a linear least-squares fit on the following data, once with the intercept fixed at 2.00 and once without specifying the intercept:

x	0	1	2	3	4	5
y	2.10	2.99	4.01	4.99	6.01	6.98

Compare your slopes and your correlation coefficients for the two fits.

16.3 DATA REDUCTION WITH A DERIVATIVE

In an earlier section, we performed an approximate integration on the Clapeyron equation in order to obtain the Clausius-Clapeyron equation, which could be fitted to a linear function. If we have a set of data and do not have a theoretical formula with which to linearize the data, we sometimes work directly with the data. For example, pretend that we do not know how to linearize the data in Table 16.1 and want to work directly with the Clapeyron equation. We need to evaluate the derivative dP/dT in order to find the value of ΔH_m. We produce a new graph using Excel. This graph is shown in Figure 16.3. There are procedures for "smoothing" data and evaluating the derivative numerically,[11] but we will not discuss them. Instead, we start with a nonlinear fit to the data as given. Such data points can usually be fit quite closely with a polynomial over a restricted range of values of the independent variable.

Example 16.12. Fit the data in Table 16.1 to a fourth-degree polynomial. Obtain a formula for the derivative dP/dT. Evaluate the derivative for 45 °C and use this value to calculate the molar enthalpy change of vaporization.

[11] C.W. Garland, J.W. Nibler and D.P. Shoemaker, *Experiments in Physical Chemistry*, 7th ed., pp. 770ff, MJcGraw-Hill, Boston, 2003.

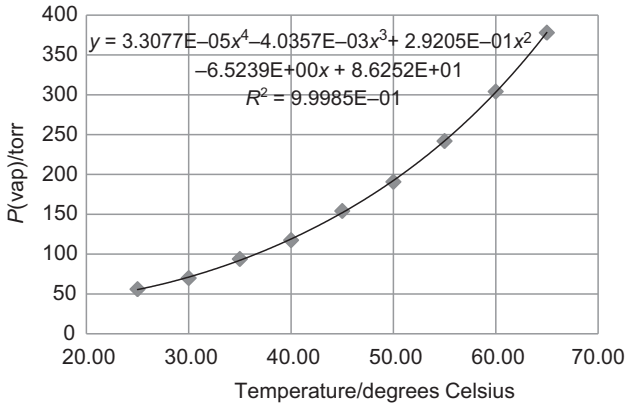

FIGURE 16.3 The vapor pressure of ethanol as a function of the Celsius temperature.

From a least-squares fit on a graph using Excel, the polynomial is

$$P/torr = 3.3077 \times 10^{-5}t^4 - 4.0357 \times 10^{-2}t^3 + 2.9205 \times 10^{-1}t^2 - 6.5239t + 86.252, \tag{16.73}$$

where t represents the Celsius temperature and where we omit the units. The correlation coefficient was equal to 0.99985, corresponding to a close fit. Differentiation of this formula gives

$$\frac{dP}{dt} = 1.32308 \times 10^{-4}t^3 - 1.2107 \times 10^{-1}t^2 + 5.8140 \times 10^{-1}t - 6.5239.$$

Evaluation of this expression for t = 45 °C gives $dP/dt = 7.341$ torr °C^{-1}. Since the kelvin and the degree Celsius have equal size, this is equivalent to $dP/dT = 7.341$ torr K^{-1}. As in the integration of the Clapeyron equation, we make the approximation that $\Delta V_m \approx V_m(\text{gas}) \approx RT/P$ and that the molar volume of the liquid is negligible. At 45 °C

$$\Delta V_m \approx V_m(\text{gas}) \approx \frac{RT}{P} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(318.15 \text{ K})}{154.1 \text{ torr}} \left(\frac{760 \text{ torr}}{101325 \text{ J m}^{-3}}\right) = 0.1288 \text{ m}^3 \text{ mol}^{-1}.$$

From the Clapeyron equation

$$\Delta H_m = (T\Delta V_m)\left(\frac{dP}{dT}\right),$$

$$\Delta H_m = (318.15 \text{ K})(0.1287 \text{ m}^3 \text{ mol}^{-1})(7.341 \text{ torr K}^{-1}) \left(\frac{101325 \text{ J m}^{-3}}{760 \text{ torr}}\right) = 4.007 \times 10^4 \text{ J mol}^{-1} = 40.07 \text{ kJ mol}^{-1}.$$

This value compares with the value from the linear least-squares fit to the Clausius-Clapeyron equation, 40.36 kJ mol^{-1}, and the accepted value of 40.3 kJ mol^{-1}.

Exercise 16.13. Fit the data of the previous example to a quadratic function (polynomial of degree 2) and repeat the calculation.

PROBLEMS

1. In order to determine the intrinsic viscosity $[\eta]$ of a solution of polyvinyl alcohol, the viscosities of several solutions with different concentrations are measured. The intrinsic viscosity is defined as the limit[12]

$$\lim_{c\to 0}\left(\frac{1}{c}\ln\left(\frac{\eta}{\eta_0}\right)\right),$$

where c is the concentration of the polymer measured in grams per deciliter, η is the viscosity of a solution of concentration c, and η_0 is the viscosity of the pure solvent (water in this case). The intrinsic viscosity and the viscosity-average molar mass are related by the formula

$$[\eta] = (2.00 \times 10^{-4} \text{dl g}^{-1})\left(\frac{M}{M_0}\right)^{0.76},$$

where M is the molar mass and $M_0 = 1$ g mol^{-1} (1 dalton). Find the molar mass if $[\eta] = 0.86$ dl g^{-1}. Find the expected error in the molar mass if the expected error in $[\eta]$ is 0.03 dl g^{-1}.

2. Assuming that the ideal gas law holds, find the amount of nitrogen gas in a container if

$$P = 0.836 \text{ atm} \pm 0.003 \text{ atm},$$
$$V = 0.01985 \text{ m}^3 \pm 0.00008 \text{ m}^3,$$
$$T = 298.3 \text{ K} \pm 0.2 \text{ K}.$$

Find the expected error in the amount of nitrogen.

3. The van der Waals equation of state is

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT.$$

For carbon dioxide, $a = 0.3640$ Pa m^6 mol^{-1} and $b = 4.267 \times 10^{-5}$ m^3 mol^{-1}. Find the pressure of 0.7500 mol of carbon dioxide if $V = 0.0242$ m^3 and $T = 298.0$ K. Find the uncertainty in the pressure if the uncertainty in the volume is

[12] Carl W. Garland, Joseph W. Nibler, and David P. Shoemaker, *Experiments in Physical Chemistry*, 7th ed., McGraw-Hill, New York, 2003, pp. 321–323.

0.00004 m^3 and the uncertainty in the temperature is 0.5 K. Assume that the uncertainty in n is negligible. Find the pressure predicted by the ideal gas equation of state. Compare the difference between the two pressures you calculated and the expected error in the pressure.

4. The following is a set of student data on the vapor pressure of liquid ammonia, obtained in a physical chemistry laboratory course.

(a) Find the indicated enthalpy change of vaporization.

Temperature (°C)	Pressure (Torr)
−76.0	51.15
−74.0	59.40
−72.0	60.00
−70.0	75.10
−68.0	91.70
−64.0	112.75
−62.0	134.80
−60.0	154.30
−58.0	176.45
−56.0	192.90

(b) Ignoring the systematic errors, find the 95% confidence interval for the enthalpy change of vaporization.

5. The vibrational contribution to the molar heat capacity of a gas of nonlinear molecules is given in statistical mechanics by the formula

$$C_m(\text{vib}) = R \sum_{i=1}^{3n-6} \frac{u_i^2 e^{-u_i}}{(1 - e^{-u_i})^2},$$

where $u_i = h\nu_i/k_B T$. Here ν_i is the frequency of the ith normal mode of vibration, of which there are $3n - 6$ if n is the number of nuclei in the molecule, h is Planck's constant, k_B is Boltzmann's constant, R is the ideal gas constant, and T is the absolute temperature. The H_2O molecule has three normal modes. The frequencies are given by

$$\nu_1 = 4.78 \times 10^{13}\ \text{s}^{-1} \pm 0.003 \times 10^{13}\ \text{s}^{-1},$$
$$\nu_2 = 1.095 \times 10^{14}\ \text{s}^{-1} \pm 0.004 \times 10^{14}\ \text{s}^{-1},$$
$$\nu_3 = 1.126 \times 10^{14}\ \text{s}^{-1} \pm 0.005 \times 10^{14}\ \text{s}^{-1}.$$

Calculate the vibrational contribution to the heat capacity of H_2O vapor at 500.0 K and find the 95% confidence interval.Assume the temperature to be fixed without error.

6. Water rises in a clean glass capillary tube to a height h given by

$$h + \frac{r}{3} = \frac{2\gamma}{\rho g r},$$

where r is the radius of the tube, ρ is the density of water, equal to 998.2 kg m^{-3} at 20 °C, g is the acceleration due to gravity, equal to 9.80 m s^{-2}, h is the height to the bottom of the meniscus, and γ is the surface tension of the water. The term $r/3$ corrects for the liquid above the bottom of the meniscus.

(a) If water at 20 °C rises to a height h of 29.6 mm in a tube of radius r = 0.500 mm, find the value of the surface tension of water at this temperature.

(b) If the height h is uncertain by 0.4 mm and the radius of the capillary tube is uncertain by 0.02 mm, find the uncertainty in the surface tension.

(c) The acceleration due to gravity varies with latitude. At the poles of the earth it is equal to 9.83 m s^{-2}. Find the error in the surface tension of water due to using this value rather than 9.80 m s^{-2}, which applies to latitude 38°.

7. Vaughan[13] obtained the following data for the dimerization of butadiene at 326 °C.

Time (min)	Partial pressure of butadiene (atm)
0	to be deduced
3.25	0.7961
8.02	0.7457
12.18	0.7057
17.30	0.6657
24.55	0.6073
33.00	0.5573
42.50	0.5087
55.08	0.4585
68.05	0.4173
90.05	0.3613
119.00	0.3073
259.50	0.1711
373.00	0.1081

Determine whether the reaction is first, second, or third order. Find the rate constant, ignoring systematic errors. Find the initial pressure of butadiene.

[13] W.E. Vaughan, "The Homogeneous Thermal Polymerization of 1,3-Butadiene," *J. Am. Chem. Soc*. **54**, 3863 (1932).

8. Make a graph of the partial pressure of butadiene as a function of time, using the data in the previous problem. Find the slope of the tangent line at 33.00 min and deduce the rate constant from it. Compare with the result from the previous problem.

9. The following are (contrived) data for a chemical reaction of one substances.

Time (min)	Concentration (mol l^{-1})
0	0.500
2	0.349
4	0.267
6	0.217
8	0.182
10	0.157
12	0.139
14	0.124
16	0.112
18	0.102
20	0.093

(a) Assume that there is no appreciable back reaction and determine the order of the reaction and the value of the rate constant.

(b) Find the expected error in the rate constant at the 95% confidence level.

10. If a capacitor of capacitance C is discharged through a resistor of resistance R the voltage on the capacitor follows the formula

$$V(t) = V(0)e^{-t/RC}.$$

The following are data on the voltage as a function of time for the discharge of a capacitor through a resistance of 102 kΩ.

t (s)	V (s)
0.00	1.00
0.020	0.819
0.040	0.670
0.060	0.549
0.080	0.449
0.100	0.368
0.120	0.301
0.140	0.247
0.160	0.202
0.180	0.165
0.200	0.135

Find the capacitance and its expected error.

11. The *Bouguer–Beer law* (sometimes called the *Lambert–Beer law* or Beer's law) states that $A = alc$, where A is the of a solution, defined as $\log_{10}(I_0/I)$, where I_0 is the incident intensity of light at the appropriate wavelength and I is the transmitted intensity; l is the length of the cell through which the light passes; and c is the concentration of the absorbing substance. The coefficient a is called the *molar absorptivity* if the concentration is measured in moles per liter. The following is a set of data for the absorbance of a set of solutions of disodium fumarate at a wavelength of 250 nm.

A	0.1425	0.2865	0.4280	0.5725	0.7160	0.8575
c(mol l^{-1})	100 $\times 10^{-4}$	2.00 $\times 10^{-4}$	3.00 $\times 10^{-4}$	4.00 $\times 10^{-4}$	5.00 $\times 10^{-4}$	6.00 $\times 10^{-4}$

Using a linear least-squares fit with intercept set equal to zero, find the value of the absorptivity a if $l = 1.000$ cm. For comparison, carry out the fit without specifying zero intercept.

Appendices

APPENDIX A. VALUES OF PHYSICAL CONSTANTS[1]

Avogadro's constant,

$$N_{\mathrm{Av}} = 6.0221367 \times 10^{23}\ \mathrm{mol}^{-1}.$$

Molar ideal gas constant,

$$\begin{aligned} R &= 8.314510\ \mathrm{J\ mol^{-1}\ K^{-1}} \\ &= 0.0820578\ \mathrm{l\ atm\ K^{-1}\ mol^{-1}} \\ &= 1.9872\ \mathrm{cal\ K^{-1}\ mol^{-1}}. \end{aligned}$$

The magnitude of an electron's charge,

$$e = 1.60217733 \times 10^{-19}\ \mathrm{C}.$$

Planck's constant,

$$h = 6.6260755 \times 10^{-34}\ \mathrm{J\ s}.$$

Boltzmann's constant,

$$k_B = 1.3806568 \times 10^{-23}\ \mathrm{J\ K^{-1}}.$$

The rest-mass of an electron,

$$m_e = 9.1093897 \times 10^{-31}\ \mathrm{kg}.$$

The rest-mass of a proton,

$$m_p = 1.6726231 \times 10^{-27}\ \mathrm{kg}.$$

The rest-mass of a neutron,

$$m_n = 1.6749286 \times 10^{-27}\ \mathrm{kg}.$$

[1] From E.G. Cohen and B.N. Taylor, "The 1986 Adjustment of the Fundamental Physical Constants," CODATA Bulletin Number 63, November 1986.

The speed of light in a vacuum (exact value, used to define the standard meter),

$$\begin{aligned} c &= 2.99792458 \times 10^{8}\ \mathrm{m\ s^{-1}} \\ &= 2.99792458 \times 10^{10}\ \mathrm{cm\ s^{-1}}. \end{aligned}$$

The acceleration due to gravity near the earth's surface (varies slightly with latitude. This value applies near the latitude of Washington, DC, USA, Seoul, Korea, or Madrid, Spain),

$$g = 9.80\ \mathrm{m\ s^{-7}}.$$

The gravitational constant,

$$G = 6.67259 \times 10^{-11}\ \mathrm{m^3\ kg^{-1}\ s^{-2}}.$$

The permittivity of a vacuum,

$$\begin{aligned} \epsilon_0 &= 8.854187817 \times 10^{-12}\ \mathrm{F\ m^{-1}} \\ &= 8.8545187817 \times 10^{-12}\ \mathrm{C^2\ N^{-1}\ m^{-2}}. \end{aligned}$$

The permeability of a vacuum (exact value, by definition),

$$\mu_0 = 4\pi \times 10^{-7}\ \mathrm{N\ A^{-2}}.$$

Some Conversion Factors

1 pound = 1 lb = 0.4535924 kg.
1 inch = 1 in. = 0.0254 m (exact value by definition).
1 calorie = 1 cal = 4.184 J (exact value by definition).
1 electron volt = 1 eV = 1.60219×10^{-19} J.
1 erg = 10^{-7} J (exact value by definition).
1 atm = 760 Torr = 101, 325 N $\mathrm{m^{-2}}$
= 101, 325 pascal (Pa)
(exact values by definition).
1 atomic mass unit = 1 u = 1.66054×10^{-27} kg.
1 horsepower = 1 hp = 745.700
Watt = 745.700 J $\mathrm{s^{-1}}$.

APPENDIX B. SOME MATHEMATICAL FORMULAS AND IDENTITIES

1. The arithmetic progression of the first order to n terms,

$$\begin{aligned} &a + (a+d) + (a+2d) + \cdots + [a + (n-1)d] \\ &\quad = na + \frac{1}{2}n(n-1)d \\ &\quad = \frac{n}{2}(1\text{st term} + n\text{th term}). \end{aligned}$$

2. The geometric progression to n terms,

$$a + ar + ar^2 + \cdots + ar^{n-1} = \frac{a(1-r^n)}{1-r}.$$

3. The definition of the arithmetic mean of $a_1, a_2, \ldots, a_n$,

$$\frac{1}{n}(a_1 + a_2 + \cdots + a_n).$$

4. The definition of the geometric mean of $a_1, a_2, \ldots, a_n$,

$$(a_1 a_2 \cdots a_n)^{1/n}.$$

5. The definition of the harmonic mean of $a_1, a_2, \ldots, a_n$: If $\bar{a}_H$ is the harmonic mean, then

$$\frac{1}{\bar{a}_H} = \frac{1}{n}\left(\frac{1}{a_1} + \frac{1}{a_2} + \frac{1}{a_3} + \cdots + \frac{1}{a_n}\right).$$

6. If

$$\begin{aligned} &a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \cdots + a_n x^n \\ &\quad = b_0 + b_1 x + b_2 x^2 + b_3 x^3 + \cdots + b_n x^n \end{aligned}$$

for all values of x, then

$$a_0 = b_0, \quad a_1 = b_1, \quad a_2 = b_2, \ldots, a_n = b_n.$$

7. $\sin^2(x) + \cos^2(x) = 1.$

8. $\tan(x) = \dfrac{\sin(x)}{\cos(x)}.$

9. $\operatorname{ctn}(x) = \dfrac{1}{\tan(x)}.$

10. $\sec(x) = \dfrac{1}{\cos(x)}.$

11. $\csc(x) = \dfrac{1}{\sin(x)}.$

12. $\sec^2(x) - \tan^2(x) = 1.$

13. $\csc^2(x) - \operatorname{ctn}^2(x) = 1.$

14. $\sin(x+y) = \sin(x)\cos(y) + \cos(x)\sin(y).$

15. $\cos(x+y) = \cos(x)\cos(y) - \sin(x)\sin(y).$

16. $\sin(2x) = 2\sin(x)\cos(x).$

17. $\cos(2x) = \cos^2(x) - \sin^2(x) = 1 - 2\sin^2(x).$

18. $\tan(x+y) = \dfrac{\tan(x) + \tan(y)}{1 - \tan(x)\tan(y)}.$

19. $\tan(2x) = \dfrac{2\tan(x)}{1 - \tan^2(x)}.$

20. $\sec^2(x) - \tan^2(x) = 1.$

21. $e^{ix} = \cos(x) + i\sin(x).$

22. $\sin(x) = \dfrac{1}{2i}(e^{ix} - e^{-ix}).$

23. $\cos(x) = \dfrac{1}{2}(e^{ix} + e^{-ix}).$

24. $\sin(x) = -\sin(-x).$

25. $\cos(x) = \cos(-x).$

26. $\tan(x) = -\tan(-x).$

27. $\sin(ix) = i\sinh(x).$

28. $\cos(ix) = \cosh(x).$

29. $\tan(ix) = i\tanh(x).$

30. $\sin(x \pm iy) = \sin(x)\cosh(y) \pm i\cos(x)\sinh(y).$

31. $\cos(x \pm iy) = \cos(x)\cosh(y) \mp i\sin(x)\sinh(y).$

32. $\cosh(x) = \dfrac{1}{2}(e^x + e^{-x}).$

33. $\sinh(x) = \dfrac{1}{2}(e^x - e^{-x}).$

34. $\tanh(x) = \dfrac{\sinh(x)}{\cosh(x)}.$

35. $\operatorname{sech}(x) = \dfrac{1}{\cosh(x)}.$

36. $\operatorname{csch}(x) = \dfrac{1}{\sinh(x)}.$

37. $\operatorname{ctnh}(x) = \dfrac{1}{\tanh(x)}.$

38. $\cosh^2(x) - \sinh^2(x) = 1.$

39. $\tanh^2(x) + \operatorname{sech}^2(x) = 1.$

40. $\operatorname{ctnh}^2(x) - \operatorname{scsh}^2(x) = 1.$

41. $\sinh(x) = -\sinh(-x).$

42. $\cosh(x) = \cosh(-x).$

43. $\tanh(-x) = -\tanh(-x).$

44. Relations obeyed by any triangle with angle A opposite side a, angle B opposite side b, and angle C opposite side c:

(a) $A + B + C = 180^\circ = \pi$ rad.

(b) $c^2 = a^2 + b^2 - 2ab\cos(C).$

(c) $\dfrac{a}{\sin(A)} = \dfrac{b}{\sin(B)} = \dfrac{c}{\sin(C)}.$

APPENDIX C. INFINITE SERIES

Part 1. Series with Constant Terms

1. $1 + \dfrac{1}{2} + \dfrac{1}{3} + \dfrac{1}{4} + \cdots = \infty.$

2. $1+\frac{1}{2^2}+\frac{1}{3^2}+\frac{1}{4^2}+\cdots=\frac{\pi^2}{6}$.

3. $1+\frac{1}{2^4}+\frac{1}{3^4}+\frac{1}{4^4}+\cdots=\frac{\pi^4}{90}$.

4. $1+\frac{1}{2^p}+\frac{1}{3^p}+\frac{1}{4^p}+\cdots=\zeta(p)$.

The function $\zeta(p)$ is called the *Riemann zeta function*. See H.B. Dwight, *Tables of Elementary and Some Higher Mathematical Functions*, 4th ed., Dover, New York, 1961, for tables of values of this function.

5. $1-\frac{1}{2}+\frac{1}{3}-\frac{1}{4}+\cdots=\ln(2)$.

6. $1-\frac{1}{2^p}+\frac{1}{3^p}+\frac{1}{4^p}+\cdots=\left(1-\frac{2}{2^\rho}\right)\zeta(p)$.

Part 2. Power Series

1. Maclaurin's series. If there is a power series in x for $f(x)$, it is

$$f(x) = f(0)+\left.\frac{\mathrm{d}f}{\mathrm{d}x}\right|_{x=0} X=\frac{1}{2!}\left.\frac{\mathrm{d}^2f}{\mathrm{d}x^2}\right|_{x=0}x^2 = \frac{1}{3!}\left.\frac{\mathrm{d}^3f}{\mathrm{d}x^3}\right|_{x=0}x^3+\cdots.$$

2. Taylor's series. If there is a power series in $x-a$ for $f(x)$, it is

$$f(x) = f(a)+\left.\frac{\mathrm{d}f}{\mathrm{d}x}\right|_{\iota=a}(x-a) +\frac{1}{2!}\left.\frac{\mathrm{d}^2f}{\mathrm{d}x^2}\right|_{x=a}(x-a^2)+\cdots.$$

In these equations $\left.\frac{\mathrm{d}f}{\mathrm{d}x}\right|_{x=a}$ means the value of the derivative $\mathrm{d}f/\mathrm{d}x$ evaluated at $x=a$.

3. If, for all values of x,

$$a_0+a_1x+a_2x^2+a_3x^3+\cdots=b_0+b_1x+b_2x^2+b_3x^3+\cdots$$

then $a_0=b_0, a_1=b_1, a_2=b_2$, etc.

4. The reversion of a series. If

$$y=ax+bx^2+cx^3+\cdots$$

and

$$x=Ay+By^2+Cy^3+\cdots,$$

then

$$A=\frac{1}{a},\quad B=-\frac{b}{a^3},\quad C=\frac{1}{a^5}(2b^2-ac)$$
$$D=\frac{1}{a^7}(5abc-a^2d-5b^3),\text{ etc.}$$

See Dwight, *Table of Integrals and Other Mathematical Data* (cited above), for more coefficients.

5. Powers of a series. If

$$S=a+bx+cx^2+\mathrm{d}x^3+\cdots$$

then

$$\begin{aligned}S^2 &= a^2+2abx+(b^2+2ac)x^2+2(ad+bc)x^3\\ &\quad+(c^2+2ae+2bd)x^4\\ &\quad+2(af+be+cd)x^5+\cdots,\\ S^{1/2} &= a^{1/2}\left[1+\frac{b}{2a}x+\left(\frac{2}{2a}-\frac{b^2}{8a^2}\right)x^2+\cdots\right],\\ S^{-1} &= a^{-1}\left[1-\frac{b}{a}x+\left(\frac{b^2}{a^2}-\frac{c}{a}\right)x^2\right.\\ &\quad\left.+\left(\frac{2bc}{a^2}-\frac{d}{a}-\frac{b^3}{a^3}\right)x^3+\cdots\right].\end{aligned}$$

6. $\sin(x)=x-\frac{x^3}{3!}+\frac{x^5}{5!}-\frac{x^7}{7!}+\cdots$

7. $\cos(x)=1-\frac{x^2}{2!}+\frac{x^4}{4!}-\frac{x^6}{6!}+\cdots$

8. $\sin(\theta+x)=\sin(\theta)+x\cos(\theta)-\frac{x^2}{2!}\sin(\theta)-\frac{x^3}{3!}\cos(\theta)+\cdots$

9. $\cos(\theta+x)=\cos(\theta)-x\sin(\theta)-\frac{x^2}{2!}\cos(\theta)+\frac{x^3}{3!}\sin(\theta)+\cdots$

10. $\sin^{-1}(x) = \arcsin(x) = x+\frac{x^3}{2\cdot3}+\frac{1\cdot3x^5}{2\cdot4\cdot5}+\frac{1\cdot3\cdot5x^7}{2\cdot4\cdot6\cdot7}+\cdots,$

where $x^2<1$. The series gives the principal value, $-\pi/2<\sin^{-1}(x)<\pi/2$.

11. $\cos^{-1}(x)=\arccos(x)=\frac{\pi}{2}-\left(x+\frac{x^3}{2\cdot3}+\frac{1\cdot3x^5}{2\cdot4\cdot5}+\cdots\right),$

where $x^2<1$.
The series gives the principal value, $0<\cos^{-1}(x)<\pi$.

12. $e^x=1+x+\frac{x^2}{2!}+\frac{x^3}{3!}+\frac{x^4}{4!}+\cdots\ (x^2<\infty)$.

13. $a^x=e^{x\ln(a)}=1+x\ln(a)+\frac{(x\ln(a))^2}{2!}+\cdots.$

14. $\ln(1+x)=x-\frac{x^2}{2}+\frac{x^3}{3}-\frac{x^4}{4}\cdots(x^2<1\text{ and }x=1)$.

15. $\ln(1-x)=-\left(x+\frac{x^2}{2}+\frac{x^3}{3}+\frac{x^4}{4}+\cdots\right)$
$(x^2<1\text{ and }x=-1)$.

16. $\sinh(x) = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \frac{x^7}{7!} + \cdots \ (x^2 < \infty)$.

17. $\cosh(x) = 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \frac{x^6}{6!} + \cdots \ (x^2 < \infty)$.

APPENDIX D. A SHORT TABLE OF DERIVATIVES[2]

In the following list, a, b, and c are constants, and e is the base of natural logarithms:

1. $\frac{\mathrm{d}}{\mathrm{d}x}(au) = a\frac{\mathrm{d}u}{\mathrm{d}x}$.

2. $\frac{\mathrm{d}}{\mathrm{d}x}(uv) = u\frac{\mathrm{d}v}{\mathrm{d}x} + v\frac{\mathrm{d}u}{\mathrm{d}x}$.

3. $\frac{\mathrm{d}}{\mathrm{d}x}(uvw) = uv\frac{dw}{\mathrm{d}x} + uw\frac{\mathrm{d}v}{\mathrm{d}x} + vw\frac{\mathrm{d}u}{\mathrm{d}x}$.

4. $\frac{\mathrm{d}(x^n)}{\mathrm{d}x} = nx^{n-1}$.

5. $\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{u}{v}\right) = \frac{1}{v}\frac{\mathrm{d}u}{\mathrm{d}x} - \frac{u}{v^2}\frac{\mathrm{d}v}{\mathrm{d}x} = \frac{1}{v^2}\left(v\frac{\mathrm{d}u}{\mathrm{d}x} - u\frac{\mathrm{d}v}{\mathrm{d}x}\right)$.

6. $\frac{\mathrm{d}}{\mathrm{d}x}f(u) = \frac{\mathrm{d}f}{\mathrm{d}u}\frac{\mathrm{d}u}{\mathrm{d}x}$, where f is some differentiable function of u and u is some differentiable function of x (the *chain rule*).

7. $\frac{\mathrm{d}^2}{\mathrm{d}x^2}f(u) = \frac{\mathrm{d}f}{\mathrm{d}u}\frac{\mathrm{d}^2u}{\mathrm{d}x^2} + \frac{\mathrm{d}^2f}{\mathrm{d}u^2}\left(\frac{\mathrm{d}u}{\mathrm{d}x}\right)^2$.

8. $\frac{\mathrm{d}}{\mathrm{d}x}\sin(ax) = a\cos(ax)$.

9. $\frac{\mathrm{d}}{\mathrm{d}x}\cos(ax) = -a\sin(ax)$.

10. $\frac{\mathrm{d}}{\mathrm{d}x}\tan(ax) = a\sec^2(ax)$.

11. $\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{ctn}(ax) = -a\csc^2(ax)$.

12. $\frac{\mathrm{d}}{\mathrm{d}x}\sec(ax) = a\sec(ax)\tan(ax)$.

13. $\frac{\mathrm{d}}{\mathrm{d}x}\csc(ax) = -a\csc(ax)\mathrm{ctn}(ax)$.

14. $\frac{\mathrm{d}}{\mathrm{d}x}\sin^{-1}\left(\frac{x}{a}\right) = \frac{\mathrm{d}}{\mathrm{d}x}\arcsin\left(\frac{x}{a}\right) = \frac{1}{\sqrt{a^2 - x^2}}$ if x/a is in the first or fourth quadrant $= \frac{-1}{\sqrt{a^2 - x^2}}$ if x/a is in the second or third quadrant.

15. $\frac{\mathrm{d}}{\mathrm{d}x}\cos^{-1}\left(\frac{x}{a}\right) = \frac{\mathrm{d}}{\mathrm{d}x}\arccos\left(\frac{x}{a}\right) = \frac{-1}{\sqrt{a^2 - x^2}}$ if x/a is in the first or second quadrant $= \frac{1}{\sqrt{a^2 - x^2}}$ if x/a is in the third or fourth quadrant.

16. $\frac{\mathrm{d}}{\mathrm{d}x}\tan^{-1}\left(\frac{x}{a}\right) = \frac{\mathrm{d}}{\mathrm{d}x}\arctan\left(\frac{x}{a}\right) = \frac{a}{a^2 + x^2}$.

17. $\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{ctn}^{-1}\left(\frac{x}{a}\right) = \frac{\mathrm{d}}{\mathrm{d}x}\mathrm{arcctn}\left(\frac{x}{a}\right) = \frac{-a}{a^2 + x^2}$.

18. $\frac{\mathrm{d}}{\mathrm{d}x}e^{ax} = ae^{ax}$.

19. $\frac{\mathrm{d}}{\mathrm{d}x}a^x = a^x\ln(a)$.

20. $\frac{\mathrm{d}}{\mathrm{d}x}a^{cx} = ca^{cx}\ln(a)$.

21. $\frac{\mathrm{d}}{\mathrm{d}x}u^y = yu^{y-1}\frac{\mathrm{d}}{\mathrm{d}x} + u^y\ln(u)\frac{\mathrm{d}}{\mathrm{d}x}$.

22. $\frac{\mathrm{d}}{\mathrm{d}x}x^X = x^x[1 + \ln(x)]$.

23. $\frac{\mathrm{d}}{\mathrm{d}x}\ln(ax) = \frac{1}{x}$.

24. $\frac{\mathrm{d}}{\mathrm{d}x}\log_a(x) = \frac{\log_a(a)}{x}$.

25. $\frac{\mathrm{d}}{\mathrm{d}q}\int_p^q f(x)\mathrm{d}x = f(q)$ if p is independent of q.

26. $\frac{\mathrm{d}}{\mathrm{d}q}\int_p^q f(x)\mathrm{d}x = -f(p)$ if q is independent of p.

APPENDIX E. A SHORT TABLE OF INDEFINITE INTEGRALS

In the following, an arbitrary constant of integration is to be added to each equation. a, b, c, g, and n are constants.

1. $\int \mathrm{d}x = x$.

2. $\int x\,\mathrm{d}x = \frac{x^2}{2}$.

3. $\int \frac{1}{x}\mathrm{d}x = \ln(|x|)$ Do not integrate from negative to positive values of x.

4. $\int x^n\,\mathrm{d}x = \frac{x^{n+1}}{n+1}$, where $n \neq -1$.

5. $\int (a + bx)^n\mathrm{d}x = \frac{(a + bx)^{n+1}}{b(n+1)}$.

6. $\int \frac{1}{(a + bx)}\mathrm{d}x = \frac{1}{b}\ln(|a + bx|)$.

7. $\int \frac{1}{(a + bx)^n}\mathrm{d}x = \frac{-1}{(n-1)b(a + bx)^{n-1}}$.

8. $\int \frac{x}{(a + bx)}\mathrm{d}x = \frac{1}{b^2}\left[(a + bx) - a\ln(|a + bx|)\right]$.

9. $\int \frac{a + bx}{c + gx}\mathrm{d}x = \frac{bx}{g} + \frac{ag - bc}{g^2}\ln(|c + gx|)$.

10. $\int \frac{1}{(a + bx)(c + gx)}\mathrm{d}x = \frac{1}{ag - bc}\ln\left(\left|\frac{c + gx}{cx + bx}\right|\right)$.

11. $\int \frac{1}{a^2 + x^2}\mathrm{d}x = \frac{1}{a}\tan^{-1}\left(\frac{x}{a}\right) = \frac{1}{a}\arctan\left(\frac{x}{a}\right)$.

[2] These formulas, and the other material in Appendices 3–7, are from H.B. Dwight, *Tables of Integrals and other Mathematical Data*, 4th ed., Macmillan, New York, 1961.

12. $\int \frac{x}{a^2+x^2}\mathrm{d}x = \frac{1}{2}\ln(a^2+x^2).$

13. $\int \frac{x^2}{a^2+x^2}\mathrm{d}x = x - a\tan^{-1}\left(\frac{x}{a}\right) = x - a\arctan\left(\frac{x}{a}\right).$

14. $\int \frac{x}{(a^2+x^2)^2}\mathrm{d}x = \frac{-1}{2(a^2+x^2)}.$

15. $\int \frac{1}{(a^2-b^2x^2)}\mathrm{d}x = \frac{1}{2ab}\ln\left(\left|\frac{a+bx}{a-bx}\right|\right).$

16. $\int \frac{x}{(a^2-x^2)}\mathrm{d}x = -\frac{1}{2}\ln(|a^2-x^2|).$

17. $\int \frac{x^{1/2}}{(a^2+b^2x)}\mathrm{d}x = \frac{2x^{1/2}}{b^2} - \frac{2a}{b^3}\tan^{-1}\left(\frac{bx^{1/2}}{a}\right).$

18. $\int \frac{1}{(a+bx^2)^{\rho/2}}\mathrm{d}x = \frac{-2}{(p-2)b(a+bx)^{(\rho-2)/2}}.$

19. $\int \frac{1}{(x^2+a^2)^{1/2}}\mathrm{d}x = \ln(x+(x^2+a^2)^{1/2}).$

20. $\int \frac{x}{(x^2+a^2)^{1/2}}\mathrm{d}x = (x^2+a^2)^{1/2}.$

21. $\int \frac{1}{(x^2-a^2)^{1/2}}\mathrm{d}x = \ln(x+(x^2-a^2)^{1/2}).$

22. $\int \frac{x}{(x^2-a^2)^{1/2}}\mathrm{d}x = (x^2-a^2)^{1/2}.$

23. $\int \sin(ax)\mathrm{d}x = -\frac{1}{a}\cos(ax).$

24. $\int \sin(a+bx)\mathrm{d}x = -\frac{1}{b}\cos(a+bx).$

25. $\int x\sin(x)\mathrm{d}x = \sin(x) - x\cos(x).$

26. $\int x^2\sin(x)\mathrm{d}x = 2x\sin(x) - (x^2-2)\cos(x).$

27. $\int \sin^2(x)\mathrm{d}x = \frac{x}{2} - \frac{\sin(2x)}{4} = \frac{x}{2} - \frac{\sin(x)\cos(x)}{2}.$

28. $\int x\sin^2(x)\mathrm{d}x = \frac{x^2}{4} - \frac{x\sin(2x)}{4} - \frac{\cos(2x)}{8}.$

29. $\int \frac{1}{1+\sin(x)}\mathrm{d}x = -\tan\left(\frac{\pi}{4} - \frac{x}{2}\right).$

30. $\int \cos(ax)\mathrm{d}x = \frac{1}{a}\sin(ax).$

31. $\int \cos(a+bx)\mathrm{d}x = \frac{1}{b}\sin(a+bx).$

32. $\int x\cos(x)\mathrm{d}x = \cos(x) + x\sin(x).$

33. $\int x^2\cos(x)\mathrm{d}x = 2x\cos(x) + (x^2-2)\sin(x).$

34. $\int \cos^2(x)\mathrm{d}x = \frac{x}{2} + \frac{\sin(2x)}{4} = \frac{x}{2} + \frac{\sin(x)\cos(x)}{2}.$

35. $\int x\cos^2(x)\mathrm{d}x = \frac{x^2}{4} + \frac{x\sin(2x)}{4} + \frac{\cos(2x)}{8}.$

36. $\int \frac{1}{1+\cos(x)}\mathrm{d}x = \tan\left(\frac{x}{2}\right).$

37. $\int \sin(x)\cos(x)\mathrm{d}x = \frac{\sin^2(x)}{2}.$

38. $\int \sin^2(x)\cos^2(x)\mathrm{d}x = \frac{1}{8}\left[x - \frac{\sin(4x)}{4}\right].$

39. $\int \sin^{-1}\left(\frac{x}{a}\right)\mathrm{d}x = x\sin^{-1}\left(\frac{x}{a}\right) + (a^2-x^2)^{1/2}.$

40. $\int \left[\sin^{-1}\left(\frac{x}{a}\right)\right]^2\mathrm{d}x = x\left[\sin^{-1}\left(\frac{x}{a}\right)\right]^2 - 2x + 2(a^2-x^2)^{1/2}\sin^{-1}\left(\frac{x}{a}\right).$

41. $\int \cos^{-1}\left(\frac{x}{a}\right)\mathrm{d}x = x\cos^{-1}\left(\frac{x}{a}\right) - (a^2-x^2)^{1/2}.$

42. $\int \left[\cos^{-1}\left(\frac{x}{a}\right)\right]^2\mathrm{d}x = x\left[\cos^{-1}\left(\frac{x}{a}\right)\right]^2 - 2x - 2(a^2-x^2)^{1/2}\cos^{-1}\left(\frac{x}{a}\right).$

43. $\int \tan^{-1}\left(\frac{x}{a}\right)\mathrm{d}x = x\tan^{-1}\left(\frac{x}{a}\right) - \frac{a}{2}\ln(a^2+x^2).$

44. $\int x\tan^{-1}\left(\frac{x}{a}\right)\mathrm{d}x = \frac{1}{2}(x^2+a^2)\tan^{-1}\left(\frac{x}{a}\right) - \frac{ax}{2}.$

45. $\int e^{ax}\,\mathrm{d}x = \frac{1}{a}e^{ax}.$

46. $\int a^x\,\mathrm{d}x = \frac{a^x}{\ln(a)}.$

47. $\int x\,e^{ax}\,\mathrm{d}x = e^{ax}\left(\frac{x}{a} - \frac{1}{a^2}\right).$

48. $\int x^2\,e^{ax}\,\mathrm{d}x = e^{ax}\left[\frac{x^2}{a} - \frac{2x}{a^2} + \frac{2}{a^3}\right].$

49. $\int e^{ax}\sin(x)\mathrm{d}x = \frac{e^{ax}}{a^2+1}[a\sin(x) - \cos(x)].$

50. $\int e^{ax}\cos(x)\mathrm{d}x = \frac{e^{ax}}{a^2+1}[a\sin(x) + \sin(x)].$

51. $\int e^{ax}\sin^2(x)\mathrm{d}x = \frac{e^{ax}}{a^2+4}\left[a\sin^2(x) - 2\sin(x)\cos(x) + \frac{2}{a}\right].$

52. $\int \ln(ax)\mathrm{d}x = x\ln(ax) - x.$

53. $\int x\ln(x)\mathrm{d}x = \frac{x^2}{2}\ln(x) - \frac{x^2}{4}.$

54. $\int \frac{\ln(ax)}{x}\mathrm{d}x = \frac{1}{2}[\ln(ax)]^2.$

55. $\int \frac{1}{x\ln(x)}\mathrm{d}x = \ln(|\ln(x)|).$

56. $\int \tan(ax)\mathrm{d}x = \frac{1}{a}\ln(|\sec(ax)|) = -\frac{1}{a}\ln(|\cos(ax)|).$

57. $\int \cot(ax)\mathrm{d}x = \frac{1}{a}\ln(|\sin(ax)|).$

APPENDIX F. A SHORT TABLE OF DEFINITE INTEGRALS

In the following list, a, b, m, n, p, and r are constants:

1. $$\int_0^\infty x^{n-1}\, e^{-x}\, \mathrm{d}x \;=\; \int_0^1 \left[\ln\left(\frac{1}{x}\right)\right]^{-1} \mathrm{d}x \;=\; \Gamma(n)$$
$(n > 0)$.

The function $\Gamma(n)$ is called the *gamma function*. It has the following properties: for any $n > 0$,

$$\Gamma(n+1) = n\Gamma(n)$$

for any integral value of $n > 0$,

$$\Gamma(n) = (n-1)!$$

for n not an integer,

$$\Gamma(n)\Gamma(1-n) = \frac{\pi}{\sin(n\pi)},$$

$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}.$$

2. $$\int_0^\infty \frac{1}{1+x+x^2}\mathrm{d}x = \frac{\pi}{3\sqrt{3}}.$$

3. $$\int_0^\infty \frac{x^{p-1}}{(1+x)^\rho}\mathrm{d}x = \frac{\pi}{\sin(p\pi)} \quad (0 < p < 1).$$

4. $$\int_0^\infty \frac{x^{p-1}}{a+x}\mathrm{d}x = \frac{\pi a^{p-1}}{\sin(p\pi)} \quad (0 < p < 1).$$

5. $$\int_0^\infty \frac{x^p}{(1+ax)^2}\mathrm{d}x = \frac{p\pi}{a^{\rho+1}\sin(p\pi)}.$$

6. $$\int_0^\infty \frac{1}{1+x^p}\mathrm{d}x = \frac{\pi}{p\sin(\pi/p)}.$$

7. $$\int_0^\pi \cos(mx)\cos(nx)\mathrm{d}x = \begin{cases} 0 & \text{if } m \neq n \\ \dfrac{\pi}{2} & \text{if } m = n \end{cases} \qquad (m,n \text{ integers})$$

8. $$\int_0^\pi \sin(mx)\sin(nx)\mathrm{d}x = \begin{cases} 0 & \text{if } m = n \\ 0 & \text{if } m \neq n \text{ and } m+n \text{ is even} \\ \dfrac{2m}{m^2-n^2} & \text{if } m \neq n \text{ and } m+n \text{ is odd} \\ & (m,n \text{ integers}). \end{cases}$$

9. $$\int_0^\infty \sin\left(\frac{\pi x^2}{2}\right)\mathrm{d}x = \int_0^\infty \cos\left(\frac{\pi x^2}{2}\right)\mathrm{d}x = 1/2.$$

10. $$\int_0^\infty \sin(x^p)\mathrm{d}x = \Gamma\left(1+\frac{1}{p}\right)\sin\left(\frac{\pi}{2p}\right) \quad (p > 1).$$

11. $$\int_0^\infty \cos(x^p)\mathrm{d}x = \Gamma\left(1+\frac{1}{p}\right)\cos\left(\frac{\pi}{2p}\right) \quad (p > 1).$$

12. $$\int_0^\infty \frac{\sin(mx)}{x}\mathrm{d}x = \begin{cases} \dfrac{\pi}{2} & \text{if } m > 0 \\ 0 & \text{if } m = 0 \\ -\dfrac{\pi}{2} & \text{if } m < 0 \end{cases}.$$

13. $$\int_0^\infty \frac{\sin(mx)}{x^\rho}\mathrm{d}x = \frac{\pi m^{p-1}}{2\sin(p\pi/2)\Gamma(p)} \qquad (0 < p < 2,\ m > 0)\ .$$

14. $$\int_0^\infty \frac{\cos(mx)}{a^2+x^2}\mathrm{d}x = \frac{\pi}{2a}e^{-ma}.$$

15. $$\int_0^\infty e^{-ax}\,\mathrm{d}x = \frac{1}{a} \quad (a > 0).$$

16. $$\int_0^\infty x\, e^{-ax}\,\mathrm{d}x = \frac{1}{a^2} \quad (a > 0).$$

17. $$\int_0^\infty x^2\, e^{-ax}\,\mathrm{d}x = \frac{2}{a^3} \quad (a > 0).$$

18. $$\int_0^\infty x^{1/2}\, e^{-ax}\,\mathrm{d}x = \frac{\sqrt{\pi}}{2a^{3/2}} \quad (a > 0).$$

19. $$\int_0^\infty e^{-r^2x^2}\,\mathrm{d}x = \frac{\sqrt{\pi}}{2r} \quad (r > 0).$$

20. $$\int_0^\infty x\, e^{-r^2x^2}\,\mathrm{d}x = \frac{1}{2r^2} \quad (r > 0).$$

21. $$\int_0^\infty x^2\, e^{-r^2x^2}\,\mathrm{d}x = \frac{\sqrt{\pi}}{4r^3} \quad (r > 0).$$

22. $$\int_0^\infty x^{2n+1}\, e^{-r^2x^2}\,\mathrm{d}x = \frac{n!}{2r^{2n+2}} \qquad (r > 0,\ n = 1, 2, \ldots).$$

23. $$\int_0^\infty x^{2n}\, e^{-r^2x^2}\,\mathrm{d}x = \frac{(1)(3)(5)\cdots(2n-1)}{2^{n+1}r^{2n+1}}\sqrt{\pi} \qquad (r > 0,\ n = 1, 2, \ldots).$$

24. $$\int_0^\infty x^a\, e^{-(rx)^b}\,\mathrm{d}x = \frac{1}{br^{a+1}}\Gamma\left(\frac{a+1}{b}\right) \qquad (a+1 > 0,\ r > 0,\ b > 0).$$

25. $$\int_0^\infty \frac{e^{-ax}-e^{-bx}}{x}\mathrm{d}x = \ln\left(\frac{b}{a}\right).$$

26. $$\int_0^\infty e^{-ax}\sin(mx)\mathrm{d}x = \frac{m}{a^2+m^2} \quad (a > 0).$$

27. $$\int_0^\infty x\, e^{-ax}\sin(mx)\mathrm{d}x = \frac{2am}{(a^2+m^2)^2} \quad (a > 0).$$

28. $$\int_0^\infty x^{p-1}\, e^{-ax}\sin(mx)\mathrm{d}x = \frac{\Gamma(p)\sin(p\theta)}{(a^2+m^2)^{p/2}}$$
$(a > 0,\ p > 0,\ m > 0)$, where $\sin(\theta) = m/r$, $\cos(\theta) = a/r$, $r = (a^2+m^2)^{1/2}$.

29. $\displaystyle\int_0^\infty e^{-ax}\cos(mx)\mathrm{d}x = \frac{a}{a^2+m^2}\ (a>0).$

30. $\displaystyle\int_0^\infty x\,e^{-ax}\cos(mx)\mathrm{d}x = \frac{a^2-m^2}{(a^2+m^2)^2}\ (a>0).$

31. $\displaystyle\int_0^\infty \frac{e^{-ax}}{x}\sin(mx)\mathrm{d}x = \arctan\left(\frac{k}{a}\right).$

32. $\displaystyle\int_0^\infty x^{p-1}\,e^{-ax}\cos(mx)\mathrm{d}x = \frac{\mathbf{\Gamma}(p)\cos(p\theta)}{(a^2+m^2)^{\rho/2}}$
$(a>0, p>0)$, where θ is the same as given in Eq. (28).

33. $\displaystyle\int_0^\infty \frac{e^{-ax}}{x}\sin(mx)\mathrm{d}x = \tan^{-1}\left(\frac{m}{a}\right)\ (a>0).$

34. $\displaystyle\int_0^\infty \frac{e^{-ax}}{x}[\cos(mx)-\cos(nx)]\mathrm{d}x$
$\displaystyle= \frac{1}{2}\ln\left(\frac{a^2+n^2}{a^2+m^2}\right)\ (a>0).$

35. $\displaystyle\int_0^\infty e^{-ax}\cos^2(mx)\mathrm{d}x = \frac{a^2+2m^2}{a(a^2+4m^2)}\ (a>0).$

36. $\displaystyle\int_0^\infty e^{-ax}\sin^2(mx)\mathrm{d}x = \frac{2m^2}{a(a^2+4m^2)}\ (a>0).$

37. $\displaystyle\int_0^\infty e^{-ax^2}\cos(kx)\mathrm{d}x = \frac{\sqrt{\pi}}{2\sqrt{a}}e^{-k^2/(4a)}.$

38. $\displaystyle\int_0^\infty e^{-ax}\sin(mx)\sin(nx)\mathrm{d}x$
$\displaystyle= \frac{2amn}{[a^2+(m-n)^2][a^2+(m+n)^2]}.$

39. $\displaystyle\int_0^\infty e^{-ax}\sin(mx)\cos(nx)\mathrm{d}x$
$\displaystyle= \frac{m(a^2+m^2-n^2)}{[a^2+(m-n)^2][a^2+(m+n)^2]}.$

40. $\displaystyle\int_0^\infty e^{-ax}\cos(mx)\cos(nx)\mathrm{d}x$
$\displaystyle= \frac{a(a^2+m^2+n^2)}{[a^2+(m-n)^2][a^2+(m+n)^2]}.$

41. $\displaystyle\int_0^\infty x\,e^{-ax}\cos(mx)\mathrm{d}x = \frac{a^2-m^2}{(a^2+m^2)^2}.$

42. $\displaystyle\int_0^\infty x\,e^{-a^2x^2}\sin(mx)\mathrm{d}x = \frac{m\sqrt{\pi}}{4a^3}e^{-m^2/(4a^2)}.$

43. $\displaystyle\int_0^\infty e^{-ax}\cos^2(mx)\mathrm{d}x = \frac{a^2+2m^2}{a(a^2+2m^2)}.$

44. $\displaystyle\int_0^\infty e^{-ax}\sin^2(mx)\mathrm{d}x = \frac{2m^2}{a(a^2+2m^2)}.$

45. $\displaystyle\int_0^1\left[\ln\left(\frac{1}{x}\right)\right]^q\mathrm{d}x = \mathbf{\Gamma}(q+1)\ (q+1>0).$

46. $\displaystyle\int_0^1 x^p\ln\left(\frac{1}{x}\right)\mathrm{d}x = \frac{1}{(p+1)^2}\ (p+1>0).$

47. $\displaystyle\int_0^1 x^p\left[\ln\left(\frac{1}{x}\right)\right]^q\mathrm{d}x = \frac{\mathbf{\Gamma}(q+1)}{(p+1)^{q+1}}$
$(p+1>0,\ q+1>0).$

48. $\displaystyle\int_0^1\ln(1-x)\mathrm{d}x = -1.$

49. $\displaystyle\int_0^1 x\ln(1-x)\mathrm{d}x = \frac{-3}{4}.$

50. $\displaystyle\int_0^1\ln(1+x)\mathrm{d}x = 2\ln(2)-1.$

51. $\displaystyle\int_0^\pi \sin^2(mx)\mathrm{d}x = \int_0^\pi \cos^2(mx)\mathrm{d}x = \frac{\pi}{2}$
$(m=1,2,\ldots).$

52. $\displaystyle\int_0^\pi \sin(mx)\sin(nx)\mathrm{d}x$
$\displaystyle= \begin{cases} 0 & \text{if } m \neq n \\ \dfrac{\pi}{2} & \text{if } m=n \end{cases}$ (m, n integers).

53. $\displaystyle\int_0^\pi \sin^m(x)\cos(mx)\mathrm{d}x$
$\displaystyle= \frac{\pi}{2^m}\cos\left(\frac{m\pi}{2}\right).$

54. $\displaystyle\int_0^\pi \sin^m(x)\sin(mx)\mathrm{d}x = \frac{\pi}{2^m}\sin\left(\frac{m\pi}{2}\right).$

55. $\displaystyle\int_0^\pi \cos^2(x)\cos\left(mx\right)\mathrm{d}x$
$\displaystyle= \frac{\pi}{4}\frac{2}{\Gamma\left(\frac{2+m}{2}+1\right)\Gamma\left(\frac{2-m}{2}+1\right)}.$

56. $\displaystyle\int_0^{\pi/2}\tan^p(x)\mathrm{d}x = \int_0^{\pi/2}\mathrm{ctn}^p(x)\mathrm{d}x$
$\displaystyle= \frac{\pi}{2\cos(p\pi/2)}\ (p^2<1).$

57. $\displaystyle\int_0^{\pi/2}\frac{x}{\tan(x)}\mathrm{d}x = \frac{\pi}{2}\ln(2).$

58. $\displaystyle\int_0^{\pi/2}\sin^p(x)\cos^p(x)\mathrm{d}x$
$\displaystyle= \frac{\mathbf{\Gamma}((p+1)/2)\mathbf{\Gamma}((q+1)/2)}{2\mathbf{\Gamma}((p+q)/2+1)}$
$(p+1>0,\ q+1>0).$

59. $\displaystyle\int_0^{\pi/2}\sin^2(mx)\mathrm{d}x = \int_0^{\pi/2}\cos^2(mx)\mathrm{d}x = \frac{\pi}{4}$
$(m=1,2,\ldots).$

APPENDIX G. SOME INTEGRALS WITH EXPONENTIALS IN THE INTEGRANDS: THE ERROR FUNCTION

We begin with the integral

$$\int_0^\infty e^{-x^2}\,dx = 1.$$

We compute the value of this integral by a trick, squaring the integral and changing one variable:

$$I^2 = \left[\int_0^\infty e^{-x^2}\,dx\right]^2 = \int_0^\infty e^{-x^2}\,dx \int_0^\infty e^{-y^2}\,dy = \int_0^\infty \int_0^\infty e^{-(x^2+y^2)},dx\,dy.$$

We now change to polar coordinates,

$$I^2 = \int_0^{\pi/2}\int_0^\infty e^{-\rho^2}\,\rho\,d\rho\,d\phi = \frac{\pi}{2}\int_0^\infty e^{-\rho^2}\,\rho\,d\rho = \frac{\pi}{2}\int_0^\infty \frac{1}{2}e^{-z}\,dz = \frac{\pi}{4}.$$

Therefore,

$$I = \int_0^\infty e^{-x^2}\,dx = \frac{\sqrt{\pi}}{2}$$

and

$$\boxed{\int_0^\infty e^{-ax^2}\,dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}}. \qquad \text{(G.1)}$$

Another trick can be used to obtain the integral,

$$\int_0^\infty x^{2n}\,e^{-ax^2}\,dx,$$

where n is an integer. For $n = 1$,

$$\int_0^\infty x^2\,e^{-ax^2}\,dx = -\int_0^\infty \frac{d}{da}[e^{-ax^2}]dx = -\frac{d}{da}\int_0^\infty e^{-ax^2}\,dx = -\frac{d}{da}\left[\frac{1}{2}\sqrt{\frac{\pi}{a}}\right] = \frac{1}{4a}\sqrt{\frac{\pi}{a}} = \frac{\pi^{1/2}}{4a^{3/2}}. \qquad \text{(G.2)}$$

For n an integer greater than unity,

$$\int_0^\infty x^{2n}\,e^{-ax^2}\,dx = (-1)^n - \frac{d^n}{da^n}\left[\frac{1}{2}\sqrt{\frac{\pi}{a}}\right]. \qquad \text{(G.3)}$$

Equations (G.2) and (G.3) depend on the interchange of the order of differentiation and integration. This can be done if an improper integral is uniformly convergent. The integral in Eq. (G.1) is uniformly convergent for all real values of a greater than zero. Similar integrals with odd powers of x are easier. By the method of substitution,

$$\int_0^\infty x\,e^{-ax^2}\,dx = \frac{1}{2a}\int_0^\infty e^{-y}\,dy = \frac{1}{2a}. \qquad \text{(G.4)}$$

We can apply the trick of differentiating under the integral sign just as in Eq. (G.3) to obtain

$$\int_0^\infty x^{2n+1}\,e^{-ax^2}\,dx = (-1)^n\frac{d^n}{da^n}\left(\frac{1}{2a}\right). \qquad \text{(G.5)}$$

The integrals with odd powers of x are related to the gamma function, defined in Appendix F. For example,

$$\int_0^\infty x^{2n+1}\,e^{-x^2}\,dx = \frac{1}{2}\int_0^\infty y^n\,e^{-y}\,dy = \frac{1}{2}\Gamma(n+1). \qquad \text{(G.6)}$$

The Error Function

The indefinite integral

$$\int e^{-x^2}\,dx$$

has never been expressed as a closed form (a formula not involving an infinite series or something equivalent). The definite integral for limits other than 0 and ∞ is therefore not obtainable in closed form. Because of the frequent occurrence of such definite integrals, tables of numerical approximations have been generated.[3] One form in which the tabulation is done is as the *error function*, denoted by $\mathrm{erf}(x)$ and defined by

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^\infty e^{-t^2}\,dt.$$

As you can see from Eq. (G.1),

$$\lim_{x\to\infty}\mathrm{erf}(x) = 1.$$

The name "error function" is chosen because of its frequent use in probability calculations involving the Gaussian probability distribution. Another form giving the same information is the *normal probability integral*[4]

$$\frac{1}{\sqrt{2\pi}}\int_{-x}^{x} e^{-t^2/2}\,dt.$$

[3] Two commonly available sources are Eugene Jahnke and Fritz Emde, *Tables of Functions*. Dover, New York, 1945, and Milton Abramowitz and Irene A. Stegun, Eds., *Handbook of Mathematical Functions with Formulas, Graph, and Mathematical Tables*, US Government Printing Office, Washington, DC, 1964.

[4] Herbert B. Dwight, *Tables of Integrals and Other Mathematical Data*, 4th ed., Macmillan, New York, 1961, p. 136.

Values of the Error Function

x		0	1	2	3	4	5	6	7	8	9
0.0	0.0	000	113	226	338	451	564	676	789	901	013*
0.1	0.1	125	236	348	459	569	680	790	900	009*	118*
0.2	0.2	227	335	443	550	657	763	869	974	079*	183*
0.3	0.3	286	389	491	593	694	794	893	992	090*	187*
0.4	0.4	284	380	475	569	662	755	847	937	027*	117*
0.5	0.5	205	292	379	465	549	633	716	798	879	959
0.6	0.6	039	117	194	270	346	420	494	566	638	708
0.7		778	847	914	981	047*	112*	175*	238*	300*	361*
0.8	0.7	421	480	538	595	651	707	761	814	867	918
0.9		969	019*	068*	116*	163*	209*	254*	299*	342*	385*
1.0	0.8	427	468	508	548	586	624	661	698	733	768
1.1		802	835	868	900	931	961	991	020*	048*	076*
1.2	0.9	103	130	155	181	205	229	252	275	297	319
1.3		340	361	381	400	419	438	456	473	490	507
1.4	0.95	23	39	54	69	83	97	11*	24*	37*	49*
1.5	0.96	61	73	84	95	06*	16*	26*	36*	45*	55*
1.6	0.97	63	72	80	88	96	04*	11*	18*	25*	32*
1.7	0.98	38	44	50	56	61	67	72	77	82	86
1.8		91	95	99	03*	07*	11*	15*	18*	22*	25*
1.9	0.99	28	31	34	37	39	42	44	47	49	51
2.0	0.995	32	52	72	91	09*	26*	42*	58*	73*	88*
2.1	0.997	02	15	28	41	53	64	75	85	95	05*
2.2	0.998	14	22	31	39	46	54	61	67	74	80
2.3		86	91	97	02*	06*	11*	15*	20*	24*	28*
2.4	0.999	31	35	38	41	44	47	50	52	55	57
2.5		59	61	63	65	67	69	71	72	74	75
2.6		76	78	79	80	81	82	83	84	85	86
2.7		87	87	88	89	89	90	91	91	92	92
2.8	0.9999	25	29	33	37	41	44	48	51	54	56
2.9		59	61	64	66	68	70	72	73	75	77

* From Eugene Jahnke and Fritz Emde, *Tables of Functions*, Dover Publications, New York, 1945, p. 24.

APPENDIX H. ANSWERS TO SELECTED NUMERICAL EXERCISES AND PROBLEMS

Chapter 1

Exercises

1.2. **(a)** 2.18×10^{-18} J.
(b) 3.890×10^{4} m.

1.5. $P \approx 1.24 \times 10^{4}$ Pa.

Problems

1. 39.37 in.

3. 186282.397 mi s^{-1}.

5. $1.80261750 \times 10^{12}$ furlong fortnight^{-1}.

7. **(a)** 3.785 l.
(b) 5.9212 gal = 0.79154 ft^3.

9. 3155.695 s = 52.594920 min.

11. **(a)** 591.67 °R.
(b) 459.27 °R.

13. $0.0179\ \text{m}^3$.

15. **(a)** $0.082058\ \text{l atm K}^{-1}\ \text{mol}^{-1}$.

(b) $0.33464\ \text{atm} = 3.3907 \times 10^4\ \text{N m}^{-2}$.

17. 0.0239 °C.

19. $1.08168 \times 10^{21}\ \text{m}^3$.

21. 1.000 acre = 4047 m^2.
1.000 hectare = 2.471 acre.

Chapter 2

Exercises

2.5. **(a)** $\ln(100.000) = 4.60517$.

(b) $\ln(0.0010000) = -6.90776$.

(c) $\log_{10}(e) = 0.43429\cdots$.

2.7. 12.7 s.

2.14. 0.9954.

Problems

3. 4.74 s

5. **(a)** $\tan\big(0.600\big) = 0.684$.

(b) $\sin(0.100) = 0.100$.

(c) $\cosh(12.0) = 8 \times 10^4$.

(d) $\sinh(10.0) = 1.1 \times 10^4$.

Chapter 3

Exercises

3.3. **(a)** $x = 5.20, y = 3.00$.

(b) $\rho = 11.18, \phi = 1.107\ \text{rad} = 63.43°$.

3.4. $r = 5.39, \phi = 0.98279\ \text{rad} = 56.3°$, $\theta = 0.733\ \text{rad} = 42.0°$.

3.5. $x = 12.50, y = 50.23, z = 17.50$.

3.6. $z = 3.000, \rho = 2.828, \phi = 45°$.

3.9. **(a)** $z = 5.66e^{0.785i}$.

(b) $z = e^{\pi i}$.

3.10. **(a)** $z = 3i$.

(b) $z = -i$.

3.13. $R(z) = 5.00, I(z) = 6.00, r = 7.781$, $\phi = 0.876\ \text{rad} = 50.2°$.

3.14. $\sqrt{5.657}e^{0.3927i}, \sqrt{5.657}e^{3.534i}$.

3.15. $e^{\pi i/4}, e^{3\pi i/4}, e^{5\pi i/4}, e^{7\pi i/4}$.

Problems

3. $h = 30$ m.

7. $\rho = 5.00, \phi = 53.1° = 0.927$ rad.

11. $e^{-2.00i} + 3e^{-i\pi}$.

13. 5.00.

15. $1.316e^{\pi i/8}, 1.316e^{5\pi i/8}, 1.316e^{9\pi i/8}, 1.316e^{13\pi i/8}$.

17. $R(z) = 0.43378, I(z) = -0.18322, r = 0.47079$, $\phi = -0.3996$.

Chapter 4

Exercises

4.2. $1.50\mathbf{i} + 9.00\mathbf{j}$.

4.3. 5.66.

4.4b. $-5.00, -30.00$.

4.5a. $|\mathbf{A}| = 3.606, |\mathbf{B}| = 4.123$.

4.5b. $\mathbf{i}(5.00) + \mathbf{j}(-2.00), 5.385$.

4.5c. -14.00.

4.5d. $2.799\ \text{rad} = 160.3°$.

4.6. 7.07.

4.7a. $(2.00)\mathbf{i}$.

4.7b. 2.00.

4.7c. $74.5° = 1.300$ rad.

4.10. 7.210×10^{-19} N.

4.11. $6.41\ \text{kg m}^2\ \text{s}^{-1}$.

Problems

1. $-1.00\mathbf{i} + 2.00\mathbf{k}$.

3. 0.

5. 1.00.

7. $-2.00\mathbf{i} + 4.00\mathbf{j} - 2.00\mathbf{k}$.

9. $107° = 1.86$ rad.

11. $0.18\ \text{m s}^{-1}$.

13. 118 N.

15. $2.188 \times 10^6\ \text{m s}^{-1}; 1.094 \times 10^6\ \text{m s}^{-1}$.

Chapter 5

Exercises

5.2. $7.00 \times 10^{-6}\ \text{mol l}^{-1}$.

5.4. $1.24 \times 10^{-4}\ \text{mol l}^{-1}$.

5.6. 1.013328×10^6 Pa.

5.7. 4.491.

5.8. 5.6079.

5.9. 0.61906, 1.5123.

5.10. $x = 3.9529$.

5.14. $3.00, -1.500 + 3.4278i, -1.500 - 3.4278i$.

5.15. $x = 0, y = 0; x = \dfrac{1}{3}, y = -\dfrac{1}{3}$.

5.16. $x = \dfrac{60}{7}, y = \dfrac{50}{7}$.

5.17. $y = -\dfrac{5x}{12} = -0.4167x$.
5.18. $x = 2,\ y = 3$.

Problems

1a. 1, 2.
1b. $1, -1$.
1c. $0.500 \pm 1.323i$.
5a. 0.011 mol l^{-1}.
5b. 0.0031 mol l^{-1}.
9. 0.61906, 1.5123.
13a. 1.2×10^{-7}.
13b. 1.0002×10^{-7}.
15. $-2, -1, 2$.
17. 1.8955.
19. ± 1.4546.
21. $x = 2,\ y = 3;\ x = -3/4,\ y = 5.0625$.
23. 0.0023001 m^3 mol^{-1}.
25. $x = y = 1$.

Chapter 6

Exercises

6.1. 0.7071.
6.5. 10.00, correct values is 10.75.
6.7. 0.20871.
6.9. At $x = 0,\ K = -1$; at $x = \pi/2,\ K = 0$.
6.11. $x = \pm 0,\ \pm\pi,\ \pm 2\pi,\ \pm 3\pi, \ldots$
6.12a. Does not exist.
6.12b. Does not exist.
6.13. 1.
6.14. Does not exist.
6.15. 0.
6.16. 0.

Problems

23. $x = 100$.
25a. 0.
25b. 9/2
25c. Does not exist.
27a. 0.
27b. 1/2.
27c. 2/3.
29a. Minimum at $r = 4a_0$, maximum at $r = 0$.
29c. Minimum at $r = 3a_0$, maximum at $r = 0$.
29e. Minimum at $r = 0$ and at $r = 3a_0$, maximum at $r = 5.2361a_0$.
31. $\lambda_{\max} = \dfrac{hc}{k_B T x} = \dfrac{hc}{4.965 k_B T}$.
37a. 1.1045.
37b. 1.2757.

Chapter 7

Exercises

7.1. 5.204 m.
7.3. 1.71828.
7.4. 4.500.
7.5. 0.74682.
7.9 100.8.
7.11. 1.7183.
7.12. $\pi^2 - 4$.
7.16. 2.460; correct value is 2.4517.
7.17. 2333.3.
7.18. 2.142.

Problems

3a. 1.0017.
3b. 737.9.
5. 0.69314.
7. 90.38.
9. 0.89061.
11. 24.
13a. Diverges.
13b. 1.
15a. Diverges.
15b. Diverges.
17a. Not convergent.
17b. 0.
19. Correct value = 0.995322265 with $\Delta x = 0.100$, the result was 0.99541241.
23. 39.99 J K^{-1} mol^{-1}.
25. With 20 panels, 1444.2; correct value = 1443.1.

Chapter 8

Exercises

8.1. $\dfrac{\Delta V}{V} \approx 0.0300$; 3% error actual error 3.03%.
8.8. Not exact.
8.12. $D = 4,\ \left(\partial^2 f/\partial x^2\right)_y = -2$.

8.13a. $x = -1,\ y = 0.$
8.13b. $x = -1/2,\ y = 1/2.$
8.16. 3.558×10^{22} J.

Problems

9a. Exact.
9b. Not exact.
11a. Not exact.
11b. Exact.
15. $x = 1,\ y = 1.$
17. $f(0, 2) = 20.$

Chapter 9

Exercises

9.4. 27.
9.5. 981 J.
9.6. $w_{\text{rev}} = -1125$ J, $q_{\text{rev}} = 1125$ J.
9.7. 3π.
9.8. 19.5.
9.9. $A = 1/\pi$.
9.10. $V = \pi h a^2/3.$
9.12. 905.

Problems

1a. 8.
1b. 16/3.
3. $2\ln(2) = 1.38629.$
7. 0.002454 kg m^2.
9. 0.309 kg m^2.
13. 142.4.
15. 1885 cm^3.
17. 0.06833 kg m^2.

Chapter 10

Exercises

10.2a. S_8.
10.2b. S_{79}.
10.3. $S = 3.25889,\ S_2 = 1.693\cdots,\ S_5 = 2.73746\cdots,$ $S_{10} = 3.175461.$

Problems

1. Convergent.
3. Convergent.
10. Three terms.
11. $x = 0.14777.$
12. $x \prec 0.0861.$
19. All finite values of x.

Chapter 11

No numerical solutions.

Chapter 12

Exercises

12.1. 5.10 m.
12.4. 575.1 N m^{-1}.
12.5. 1.311×10^{-19} J.
12.9. 1.00 s, 0.3679 m.
12.15. 469 N.
12.16. 4840 m s^{-1}.

Problems

5a. 18.07 s^{-1}
5b. 0.4159 s.
11a. Not exact.
15. 20,600 y.

Chapter 13

Exercises

13.10. $(-1, -2, -3).$
13.11. $(-3. -4, -5).$

Problems

3. $i\hbar\widehat{L}_z.$
5a. 1.
5b. $a/2.$
5c. 0.
5d. $h^2/4a^2.$
9a. $(-\frac{1}{2}, \frac{1}{2}\sqrt{3}.1).$
9b. $(1, -1, -1).$
11a. $(1, -1, -1).$
11b. $(1,1, -1).$
20a. Singular.
20b. Not singular.
21a. Not singular.
21b. Not singular.

Chapter 14

Exercises

14.2 $x = 2, y = 3$.
14.3. $x_2 = 3, x_3 = 5$.
14.4. $x_1 = 1/2$.
14.5. $x_1 = -\frac{5}{2}, x_2 = 9, x_3 = \frac{11}{2}$.
14.6. $x_1 = \frac{3}{2}, x_2 = 1, x_3 = \frac{7}{2}$.
14.7. $x_1 = \frac{1}{2}, x_2 = 0, x_3 = \frac{3}{2}$.
14.8. $y = 2x$.

Problems

1. $x = 2, y = 3, z = 4$.
3. $x_1 = 3, x_2 = 4, x_3 = 6$.
5. $x_1 = 2, x_2 = 1, x_3 = 3$.
9. The eigenvalues are 0, 0, and 3.
11. The eigenvalues are 0 and 2.

Chapter 15

Exercises

15.2. 0.01084.
15.3. $\langle n \rangle = 5.000, \sigma_n = 1.581$.
15.4. $c = 0.003000, \langle x \rangle = 7.50, x_{\text{rms}} = 7.75, \sigma_x = 1.94$.
15.7. 0.8183.
15.8. $\langle p_x \rangle = 0, \langle p_x^2 \rangle = h^2/4L^2, \sigma_{p_x} = h/2L$.
15.10. 474.7 m s^{-1}.
15.11. 515.2 m s^{-1}.
15.12. 420.7 m s^{-1}.
15.13. −1.633 m.
15.14. mean = \$146,300, median = \$62,000, mode = \$41,000.
15.15. $\langle x \rangle = 2.876, s_x = 0.008$.
15.16. $\langle \alpha \rangle = 108°, s = 2.8°, \varepsilon = 3.3°$.

Problems

1. $\langle n \rangle = \frac{17.723}{3.5447} = 5.00$, $\sigma_n = 1.039$, probability = 0.722.
3. $\langle n \rangle = 5.100, \sigma_n = 1.580$.
5a. $\langle x \rangle = 3.909, \sigma_x = 2.494$.
5b. 0.6556.
7a. $\langle x \rangle = 0, \sigma_x = 3.6827$.
7b. 0.7815.
9. $M_4 = 3\sigma^4$.
11a. $\langle w \rangle = 8.499$ in., $\langle l \rangle = 11.04$ in., $s_w = 0.019$ in., $s_l = 0.023$ in.
11b. $\varepsilon_w = 0.014$ in., $\varepsilon_l = 0.016$ in.
11c. $A = 93.506$ in.^{2}
11d. $\langle A \rangle = 93.506$ in.^{2}, $s_A = 0.150$ in.^{2}
11e. $\varepsilon_A = \frac{(2.262)(0.159 \text{ in.})}{\sqrt{10}} = 0.114$ in.^{2}
13. $\overline{K} = 0.00256$ J, $\mathcal{V}_{\max} = 0.00512$ J.
15. Fifth value disregarded, mean = 68.31.

Chapter 16

Exercises

16.1. 131.69 s ± 0.21 s.
16.2. 0.21 °C.
16.3. 0.128 kg mol^{-1} ± 0.002 kg mol^{-1}.
16.4. 44.6 kJ mol^{-1}.
16.5. 0.
16.6. 0.0350 min^{-1} ± 0.0003 min^{-1}.
16.8. 0.0350 min^{-1} ± 0.002 min^{-1}.
16.9. First order, $k = 0.0537$ h^{-1}.
16.10. $k = 0.0537$ h^{-1}.
16.11. Unweighted: $m = -4752$ K, $b = 19.95$.
Weighted: $m = -4855$ K, $b = 20.28$.
16.12. With specified intercept, $y = 0.9985x + 2.00$.
Without specified intercept, $y = 0.984x + 2.0533$.
16.13. $\Delta H_m = 42.94$ kJ mol^{-1}.

Problems

1. $M = 6.25 \times 10^4$ g mol^{-1} ± 2.2×10^3 g mol^{-1}.
3. $P = 7.66 \times 10^4$ Pa ± 0.02×10^4 Pa from ideal gas equation of state, $P = 7.681 \times 10^4$ Pa. Difference = 0.02×10^4 Pa.
5. $C_m(\text{vib}) = 1.1863$ J K^{-1} mol^{-1} ± 0.0197 J K^{-1} mol^{-1}.
7. Second order, $k = 0.0206$ atm^{-1} min^{-1}, $P(0) = 0.938$ atm.
9a. Second order, $k = 0.0999$ l mol^{-1} min^{-1}.
9b. $\varepsilon_k = 0.0003$ l mol^{-1} min^{-1}.
9c. $k = 0.0968$ l mol^{-1} min^{-1}.
11. Zero intercept specified: $a = 1437$ l mol^{-1} cm^{-1}. No intercept specified: $a = 1445$ l mol^{-1} cm^{-1}.

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Additional Reading

Here is a list of some books that are useful sources for further study in mathematics to be used in chemistry. No attempt has been made to be comprehensive. Some of the books are out of print, but should be available in college and university libraries.

Books on Mathematics for Science

- M.L. Boas. *Mathematical Methods in the Physical Sciences*. John Wiley and Sons Ltd., 1967. This book is intended for student who have taken a two-semester or three-semester course in calculus and provides instruction for the topics needed in advanced chemistry, physics, and engineering courses. Although not a new book, it is still available.
- Martin C.R. Crockett, *Maths for Chemists*, Royal Society of Chemistry, 2012. This is a two-volume set, covering calculus, power series, complex numbers and linear algebra.
- Donald A. McQuarrie, *Mathematical Methods for Scientists and Engineers*, University Science Books, New York, 2003. This is an ambitious book, with over 1000 pages.
- Philip M. Morse and Herman Feshbach, *Methods of Theoretical Physics*, McGraw-Hill, New York, 1953. This book comes in two parts and is a complete survey of all of the mathematics that a scientist might need. It is out of print, but should be found in almost any college or university library.
- George Polya, *Mathematical Methods in Science* (MAA New Mathematical Library: Vol.26), The Mathematical Association of America, 1977. This book is out of print, but copies should be available on the internet. It does not focus on chemistry, but it is a very nice book, written clearly, with excellent examples from physics.
- Clifford E. Swartz, Used Math for the First Two Years of College Science, AAPT, College Park, MD, 1993. This book is a survey of various mathematical topics at the beginning college level.
- Erich Steiner, *The Chemistry Maths Book*, Oxford University Press, New York, 2008

Calculus Textbooks

- Thomas H. Barr, *Vector Calculus*, 2nd ed., Prentice Hall, Upper Saddle River, NJ, 2000. This is a textbook for a third-semester calculus course that emphasizes vector calculus.
- Wilfred Kaplan, *Advanced Calculus*, 5th ed., Addison–Wesley, Reading, MA, 2003. This is a text for a calculus course beyond the first year. It discusses infinite series and Fourier series.
- H.M. Schey, *Div, Grad, Curl, and All That: An Informal Text on Vector Calculus*, 4th ed., Norton, 2005. This book provides a clear and concise coverage of vector calculus.
- James Stewart, *Single Variable Calculus: Concepts and Contexts*, 4th ed., Brooks/Cole, Pacific Grove, CA, 2009. This is one of several calculus textbooks written by this author. It uses some examples from physics in its discussions.
- James Stewart, *Single Variable Calculus: Concepts and Contexts*, 4th ed., Brooks/Cole, Pacific Grove, CA, 2009. This is another of several calculus textbooks by this author. You can read about coordinate systems, vectors, and complex numbers in almost any calculus textbook, including this one. list new editions only

Books on Numerical Analysis

- Richard L. Burden and J. Douglas Faires, *Numerical Analysis*, Cengage Learning, 2010. This is a well-regarded numerical analysis textbook at the advanced undergraduate level. It contains numerous examples

and explicit algorithms that can be converted into computer programs.

- Robert W. Hornbeck, *Numerical Methods*, Prentice Hall, New York, 1982. This paperback book is an organized presentation of the techniques needed in physical chemistry. Although there is apparently not a newer edition, this edition is still available.

Advanced Mathematics Books

- Dean G. Duffy, *Transform Methods for Solving Partial Differential Equations*, 2nd ed., Chapman and Hall/CRC Press, Boca Raton, 2004. This book is a textbook for engineering students and focuses on practical applications.
- J.F. James, *A Student's Guide to Fourier Transforms, with Applications to Physics and Engineering*, Cambridge Univ. Press, Cambridge, UK, 2002. This book is designed to teach the subject to a student without previous knowledge of Fourier transforms. It contains a description of the fast Fourier transform method and a computer program in BASIC to carry out the transformation.
- Erwin Kreyszig, *Advanced Engineering Mathematics*, 10th ed., Wiley, New York, 2011. This book emphasizes applications rather than mathematical theory in a way that is useful to chemists as well as engineers.
- David L. Powers, *Boundary Value Problems and Partial Differential Equations*, 6th ed., Academic Press, New York, 2009. This book includes a 40-page chapter on Fourier series and integrals.

Books on Group Theory

- David M. Bishop, *Group Theory and Chemistry*, Dover Publications, 1993.
- Roy McWeeny,*Symmetry—An Introduction to Group Theory and its Applications*, Courier Dover Publications, 2002. This is a reprint of the earlier edition published by Macmillan in 1963. It presents the basic concepts of group theory and representation theory.
- Alan Vincent, *Molecular Symmetry and GroupTheory: A Programmed Introduction to Chemical Applications*, 2nd ed., John Wiley & Sons, New York, 2001. This is a very nice little book with a common-sense approach that clearly explains the basic facts and uses of group theory.

Books on Experimental Data Analysis

- R.J. Barlow, *Statistics: A Guide to the Use of Statistical Methods in the Physical Sciences*, John Wiley and Sons, Ltd., 1989. This book provides a general introduction with a number of examples.
- P.R. Bevington and D.K. Robinson, *Data Reduction and Error Analysis for the Physical Sciences*, 2nd ed., McGraw–Hill, New York, 1992. This is a very nice book, which includes a lot of useful things, including a discussion of different probability distributions, including the Gaussian distribution, and a discussion of weighted least-squares procedures.
- Carl W. Garland, Joseph W. Nibler, and David P. Shoemaker, *Experiments in Physical Chemistry*, 7th ed., McGraw–Hill, New York, 2003. This is a standard physical chemistry laboratory textbook and contains a good section on the treatment of experimental errors as well as most of the experiments commonly done in physical chemistry courses.
- John A. Rice, *Mathematical Statistics and Data Analysis*, Cengage Learning, 2007. This is a standard textbook for mathematical statistics. It includes numerous examples from experimental chemistry and is a good reference for chemists.

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- E.J. Billo, *Microsoft Excel for Chemists: A Comprehensive Guide*, 2nd ed., Wiley, New York, 2001. This is a much more useful guide to Excel than the manual provided by the manufacturer.
- Robert de Levie, *How to Use Excel in Analytical Chemistry and in General Scientific Data Analysis*, Cambridge University Press, 2001.
- Robert de Levie, *Advanced Excel for Scientific Data Analysis*, Oxford University Press, 2004. This book is available in both paperback and hardbound editions.
- Dermot Diamond and Venita C.A. Hanratty, *Spreadsheet Applications in Chemistry Using Microsoft Excel*, Wiley Interscience, New York, 1997. This is a comprehensive introduction to the use of Excel for chemists.
- Greg Harvey, *Excel 2010 for Dummies*, Wiley Publishing Co., 2010, This book is an elementary introduction to the use of Excel, Unfortunately, it is not focussed on scientific applications.
- Erwin Kreyszig and E.J. Norminton, *Mathematica Computer Manual to Accompany Advanced Engineering Mathematics*, 8th ed., Wiley, New York, 2001.
- John Walkenbach, *Microsoft Excel 2010 Bible*, Wiley Publishing Co, 2010. This book is more quite comprehensive, but it is not focussed on scientific applications.
- Stephen Wolfram, *The Mathematica Book*, 5th ed., Wolfram Media, 2003. This is a textbook that provides a complete introduction to the use of Mathematica, written by its inventor.

Problem-Solving and Problem Books

- George Polya, *How to Solve It, A New Aspect of Mathematical Method*, 2nd ed., Princeton Univ. Press, Princeton, NJ, 2004. This small book was first printed in 1957 and was out of print but has been reprinted in a 2004 edition. It contains a detailed discussion of general methods of solving problems.
- C.R. Metz, *2000 Solved Problems in Physical Chemistry*, McGraw-Hill, New York, 1990. This is a good source of practice problems in physical chemistry.

Mathematical Tables

- Milton Abramowitz and Irene A. Stegun, *Handbook of Mathematical Functions*, National Bureau of Standards, Washington DC, 1972.
- A. Erdélyi, Ed., *Tables of Integral Transforms*, Vols. I and II, McGraw–Hill, New York, 1954. This set of two volumes contains a brief introduction of several types of integral transforms, with extensive tables of transforms of specific functions.
- Herbert B. Dwight, *Tables of Integrals and Other Mathematical Data*, 4th ed., Macmillan Co., New York, 1962. This book is out of print, but if you can find a copy you will find that it is a very useful compilation of formulas, including trigonometric identities, derivatives, infinite series, and definite and indefinite integrals.
- I.S. Gradshteyn and I.M. Ryzhik, *Tables of Integrals, Series and Products*, 4th ed., prepared by Yu. V. Geronimus and M. Yu. Tseytlin, translated by Alan Jeffreys, Academic Press, New York, 1965. This is a large book with lots of definite and indefinite integrals in it. It is out of print but should be available in college and university libraries.
- The *Handbook of Chemistry and Physics*, CRC Publishing Co., Boca Raton, FL, with various editors and various editions, contains various mathematical tables.

Websites

Websites are somewhat more fluid than books, and you can probably some good ones by using a search engine such as Google. Here are a few that exist at the time of this writing:

- http://www.convertit.com/Go/Convertit/Reference/AMS55.ASP. This is the table of contents of a large compilation of mathematical tables of functions, with a link for buying the tables.
- http://en.wikibooks.org/wiki/Calculus/Taylor_series. This is like a small chapter from a calculus textbook with a discussion of Taylor series.
- Wikipedia. This is a free online encyclopedia with a lot of websites that involve applied mathematics, such as http://en.wikipedia.org/wiki/Table_of_derivatives, http://en.wikipedia.org/wiki/Table_of_integrals, and http://en.wikipedia.org/wiki/Computer_algebra_system.
- http://www.wolfram.com. This is mostly an advertisement for Mathematica and other Wolfram products.

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