

Chapter 3. Mathematical Tools

3.1. The Queen of the Sciences

We make no apology for the mathematics used in chemistry. After all, that is what classifies chemistry as a *physical science*, the grand goal of which is to reduce all knowledge to the smallest number of general statements.¹ In the sense that mathematics is logical and solvable, it forms one of the most precise and efficient languages to express concepts. Once a problem can be reduced to a mathematical statement, obtaining the desired result should be an automatic process. Thus, *many of the algorithms of chemistry are mathematical operations*. This includes extracting parameters from graphical data and solving mathematical equations for “unknown” quantities.

On the other hand we have sympathy for those who struggle with mathematical statements and manipulations. This may be in some measure due to the degree that mathematics isn't taught as algorithmic processes, procedures producing practical results. For many, a chemistry course may be the first time they have been asked to apply the mathematical techniques they learned in school to practical problems. An important point to realize in beginning chemistry is that most mathematical needs are limited to arithmetic and basic algebra.² The difficulties lie in the realm of recognition of the point at which an application crosses the

¹ Physical science is not a misnomer; chemistry owes more to physics than physics owes to chemistry. Many believe there is only *one* algorithm of chemistry. It is the mathematical wave equation first published in 1925 by the physicist Erwin Schrödinger. However it is a very difficult equation from which to extract chemical information. For all the cases where it has been solved, it has produced results that agree with experimental observations to the limit of the measurements. Until some general method can be found for solving Schrödinger's equation, or until some less difficult alternative is discovered however, chemists will continue to use the multitude of models, empirical rules and intuition that have served them in the past.

² Topics from algebra used in lower division general chemistry courses are restricted for the most part to linear, quadratic, exponential and logarithmic functions of one independent variable, systems of linear equations in several variables, and graphs. Understanding processes (changes) benefits from an acquaintance with the mathematics of change, calculus. Other topics, such as complex variables, inequalities, rational functions, matrices, and combinatorics are seldom used in introductory courses.

boundary to pure mathematics, and proficiency to derive results quickly and accurately.

Although mathematics may seem complete and perfect, in reality it is always under development and practical. *Analytic mathematical analysis* deals with exact systems and procedures, whereas *numerical analysis* treats approximations to exact systems. When “closed” solutions are not available, numerical techniques become essential.

3.2. Symbolism

Communication of ideas requires terminology. Thus each field of human activity has a characteristic terminology. Symbols are constructs intended to convey information, with communication systems being built up in hierarchical fashion, like alphabets, words and sentences in so-called “natural” (human) languages. Shorthand abbreviations, aliases, nicknames, etc. are used to impute larger meaning.³ Mathematics attempts to be a logical, precise discipline, and it should come as no surprise that certain symbols must be agreed on to communicate effectively. In arithmetic, for example, basic symbols include those representing digits (such as 0-9 in decimal notation), and certain operators (such as +, −, ×, and /). Numbers consisting of strings of digits may be combined with operators into expressions with interpretations according to the rules of arithmetic. A variety of notation conventions is possible, however. For example, “3+2” in infix notation (operation between operands) means sum the numbers three and two, as does “32+” in reverse Polish notation. Precedence and associativity conventions affect the interpretation of strings as well. For example 1+2/3 is agreed to represent $1+(2/3) = 5/3$ if multiplication takes precedence over addition (the more usual case) and means $(1+2)/3 = 1$ if addition takes precedence over multiplication (the less usual case). Also, because of the limitations of the variety of available symbols, some symbols can have multiple meanings. A common example is the minus “sign”, which used as a prefix invokes the negation operation (e.g. −3), but as an infix invokes the subtraction operation (e.g. 2 − 3). Further, mathematicians use the symbol *log* to stand for natural (base e) logarithms, while engineers may use the symbol *log* to stand for base 10 logarithms.

Pocket calculators are not immune to the above vagaries. On most calculators the EXP key does not mean exponentiation, as does the x^y key (or possibly the y^x key), but rather an explicit exponent (power) of 10. Further, in order to enter a number such as 1×10^{-14} , it may

³ “A picture is worth a thousand words.”

be sufficient to touch the keys EXP, −, 1, 4, in that order; on others EXP, ±, 1, 4 may be required, while on still others it may be necessary to enter 1, EXP, 1, 4, ± and on some calculators EXP, 1, 4, ±, may not be sufficient to avoid the value of 1×10^{-15} being entered.

Algebra introduces abstract symbols to represent quantities that can have varying values, called *variables*. Usually English or Greek (or some other language) alphabet letters are used to symbolize variables. Expressions involving variables have the same meaning as in arithmetic. Equivalencies (equations) are symbolized by an equals sign (=) connecting two expressions. Manipulation “rules” provide for the rearrangement of expressions and equations to isolate, or “solve” for particular variables (See Section 3.5).

We will occasionally use two symbols Σ and Π , commonly understood by mathematicians to represent summation and product operations, respectively. For example, Gauss’ formula for the sum of the first n integers can be represented as

$$S_n = \sum_{i=1}^{i=n} i = 1 + 2 + \cdots + n = \frac{n(n+1)}{2} \quad (3.1)$$

and the factorial formula for the product of the first n integers can be represented as

$$n! = \prod_{i=1}^{i=n} i = 1 \times 2 \times \cdots \times n \quad (3.2)$$

Another Greek letter, Δ , is commonly understood to stand for *difference*, as in the difference between two terms, such as in the case of adjacent terms in Eq. (3.1)

$$\Delta S \equiv S_{n+1} - S_n = n + 1 \quad (3.3)$$

(\equiv denotes a definition.) Note that there can be ambiguity as to which difference ΔS represents. In this case it is defined to be the “forward” difference (as distinct from the “backward” difference $S_n - S_{n-1} = n$). Science deals with measurable quantities represented by real numbers as well as integers. In this context, *we will consistently use Δ to stand for final value minus initial value*:

$\Delta X \equiv X_{\text{final}} - X_{\text{initial}} \quad (3.4)$

(where the subscripts are commonly abbreviated to their first letters).

3.3. Functions and Graphs

A fundamental event in science is cause and effect. Objects may be studied for their independent existence but the more useful information may be related to their relationship with their environment. For example, chemical substances are interesting objects, but their practical value lies in their interactions (chemical reactivities). Cause and effect relationships can be represented several ways, the most useful for our purposes being in *tables*, *graphs* and *functions*. These are symbolized using columns of numbers, pictures of points, and mathematical parenthetical notation, respectively, representing the connection between independent and dependent quantities which change, or *variables*. Functions include the *algebraic functions*, consisting of combinations of powers of variables, and *transcendental functions*, such as the *exponential function*, which is defined in terms of an infinite sum (series) of algebraic expressions (terms).

$$\exp(x) \equiv e^x = \sum_{n=0}^{n=\infty} \frac{x^n}{n!} \quad (3.5)$$

The concepts and notation of functions may be extended to multivariable (multidimensional) functions using vector notation, where \vec{x} represents a point in some given multidimensional coordinate system. The *components* of \vec{x} is the set (*array*) of values of \vec{x} projected along each axis of the coordinate system. The algebra of vectors is facilitated by associating component coordinates with *unit vectors*, \vec{e}_i along the axes of the coordinate system.

$$\vec{x} = \sum x_i \vec{e}_i \quad (3.6)$$

An alternative notation emboldens vectors: $\mathbf{x} \equiv \vec{x}$. For *orthogonal* (perpendicular if Cartesian) coordinates,

$$\vec{e}_i \vec{e}_j = \delta_{ij} \quad (3.7)$$

where $\delta_{ij} = 1$ if $i = j$ and 0 if $i \neq j$. Vectors in orthogonal coordinate systems add and (scalar) multiply component by component:

$$\vec{x} + \vec{y} = \sum (x_i + y_i) \quad (3.8a)$$

$$\vec{x} \cdot \vec{y} = \sum x_i y_i \quad (3.8b)$$

Thus the length (*magnitude*) of a vector is

$$x = \sqrt{\vec{x} \cdot \vec{x}} = \sqrt{\sum x_i^2} \quad (3.8c)$$

One of the most powerful concepts of mathematics goes back to René Descartes⁴ in the Seventeenth Century. To him is accredited the idea that *for every function there is a graph*, to which may be added *to every table there is a corresponding discrete plot*. This concept forms the basis of the process in analytical science of visualizing data and extracting theories. Data is collected, relationships summarized in cause and effect tables, the data plotted and an equation is sought to summarize the measurements and predict new observations through interpolation and extrapolation.⁵ The process of extracting a functional form from the graph may be difficult, so many times various familiar functional relationships are tried. At this level, we should be familiar with linear, parabolic and hyperbolic functional forms and their graphs. This subject is treated in more detail in the next section.

Graphs are constructed as points, curves and surfaces relative to reference lines called *axes* which are scaled to indicate units of distance along each axis. Distances are measured in units of length or angle. A point on a graph indicates a set of values for each variable equal to multiples of the distance units called the *coordinates* of the point. For example, two-variable (2D or two-dimensional) *Cartesian* graphs commonly show orthogonal x and y axes for independent and dependent variable values, whereas 2D *polar* graphs show r and θ axes representing distance and angle variable values, as shown in Fig. 3.1. Distances from origin to point are labeled with letters.

⁴ René Descartes' (French, 1596-1650) French mathematician who established the equivalence between functions and graphs (Cartesian coordinates), and began his philosophical system with the premise, "I think, therefore I am."

⁵ **Interpolation** is the process of guessing the value of a function at a point intermediate between known values. **Extrapolation** is the process of guessing the value of a function at a point outside the known values.

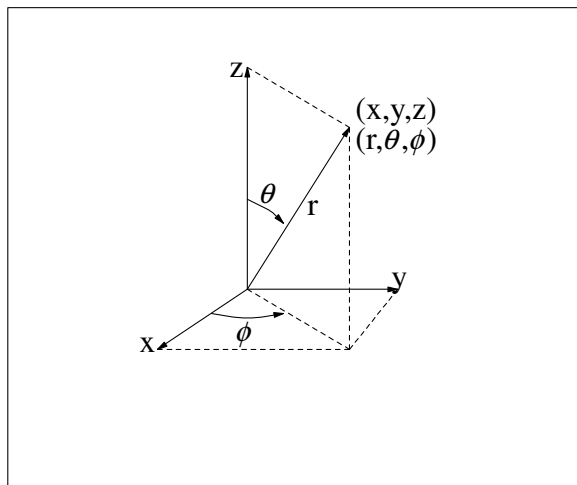


Fig. 3.1 Relationship Between Cartesian (x, y, z) and Polar (r, θ, ϕ) Coordinates

The algebraic relationship between Cartesian and polar coordinates is found by geometry and trigonometry (Section 3.10):

$$x = r \sin(\theta) \cos(\phi) \quad (3.9a)$$

$$y = r \sin(\theta) \sin(\phi) \quad (3.9b)$$

$$z = r \cos(\theta) \quad (3.9c)$$

An important property of graphs is the *slope* of a curve at a point. It represents the *rate of change* of one variable with respect to another. The slope of a straight line can be determined from two points on the line (x_1, y_1) and (x_2, y_2) in the (x, y) plane, as the ratio of the difference between the two y -values and the difference between the two x -values (“rise over run”):

$$\text{slope} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{\Delta y}{\Delta x} \quad (3.10)$$

where Δ denotes difference between two values. In fact a straight line can be defined as the set of points having a constant slope (Fig. 3.2). This is the source of the two-point formula for straight lines passing through two points (x_1, y_1) and (x_2, y_2) in the (x, y) plane:

$$\text{slope} = \frac{y - y_1}{x - x_1} = \frac{y_2 - y_1}{x_2 - x_1} \quad (3.11)$$

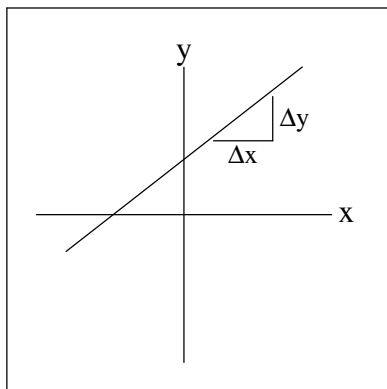


Fig. 3.2 Slope of a Straight Line

Example 3.1 Draw a graph of distance as a function of time for something traveling at a constant rate, and identify the parameters of the equation.

The basic relationship between distance and time is the *velocity* (or speed when direction is ignored), defined as the distance traveled during a given time, or *rate of change with time*, $v = d/t$. If the velocity is constant, then this equation can be rearranged to give $d = v \times t$. This expresses a *direct proportionality* between distance and time, with proportionality constant equal to the velocity. For an object moving at a constant rate, distance as a function of time would be represented by a straight line on a graph with time

as the horizontal axis and distance the vertical axis (Fig. 3.3).

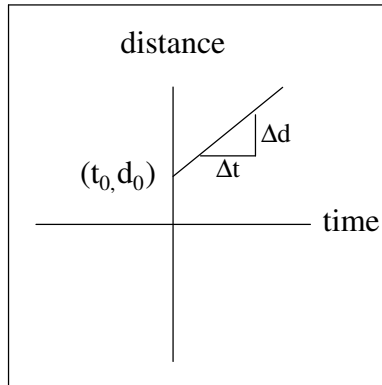


Fig. 3.3 Distance as a function of time

This example may be recognized as a special case of a general linear functional relationship, or equation of the form $y = mx + b$. The parameters m and b are related to straight line plots; m is the *slope* of the line and b is the *y-axis intercept*. In Example 3.1, the slope of the line would represent the velocity and the starting point would be the y intercept.⁶

The slope of a general curve at a given point can be approximated by the slope of a straight line tangent to the curve at that point. Alternatively, the slope of a general curve can be approximated from two points on the curve by Eq. (3.10). The closer the points, the better the approximation (for curves without wiggles in between).

⁶ What would a *negative* slope imply?

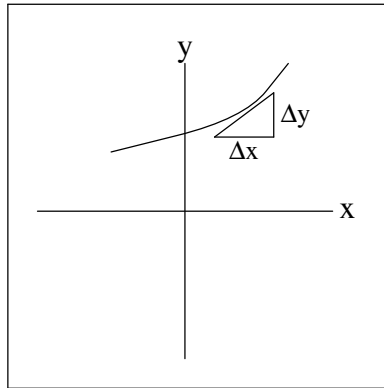


Fig. 3.4 Slope of a Curved Line

In the case of an automobile, the speed is not always constant and a plot of distance *vs* time would in general not be a straight line, or even a simple curve. A *speedometer* displays the *instantaneous rate* at a given point, represented by a tangent to the curve, while the slope of a line connecting two points of a journey represents the *average rate*.

Deriving values from functions, tables and graphs can present difficulties, particularly when they are produced from experimental data. Trying to find intermediate values (*interpolation*), values beyond the range of validity (*extrapolation*), extreme values (*maxima*, *minima*), parameters (*slopes*, *intercepts*, *curvature*), etc. can all have uncertainties due to insufficient data, uncertainty in data, rapid oscillations, etc. For these reasons automated procedures should always be suspect, and some methods for estimating accuracy and precision should accompany analyses. It never hurts to scan a visual image of the values for gross misrepresentations.

In the Algorithm for Determining the Slope of a Curve below, human judgement is needed in each step; this is appropriate in dealing with estimates and real data.

Algorithm for Determining the Slope of a Curve

Purpose: To derive the slope of a graphical, tabular or equation curve at a given point.

Procedure:

1. Inspect the curve for smoothness near the given point, either visually or numerically, or both.
 - a) Visually by scanning the graph of the curve (plotted from functional or tabular values if necessary).
 - b) Numerically by searching values for possible maxima and minima.
2. Estimate the slope either graphically or numerically, or both.
 - a) For a graphical estimate, draw a tangent straight line at the given point, select two arbitrary points on the line, and measure the x and y differences of the two points.
 - b) For numerical estimates, select pairs of points (by evaluation if functional, lookup if tabular, or reading if graphical) in the region near the given point where the graph appears to be smooth, and determine their x and y coordinate values.
3. Compute the slope as:

$$\text{slope} = \frac{y_2 - y_1}{x_2 - x_1}$$

Example 3.2 Estimate the slope of the curve of Fig. 3.4 at the point where the triangle touches the curve.

1. Visual inspection of the given curve suggests that it is acceptably smooth. (It is assumed that higher magnification would not reveal hidden wiggles.)
2. The tangent straight line has already been drawn, so it only remains to estimate its slope. Values measured on the figure appear to be 5 mm for Δy and 8 mm for Δx . (The triangle could be expanded for easier reading and possibly greater accuracy.)

3. The slope is calculated to be

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{5}{8} = 0.625$$

Note that since only relative ratio values are needed to determine slopes, absolute axis scale values are not needed (but directions from point one to point two are important for determining the sign of the slope). For the same reason, the Δx and Δy values can be measured in any units, so long as they are the same.

3.4. Curve Fitting

The process of finding an equation which matches tabular values is called *curve fitting*. Important theorems by Weierstrauss and Fourier state that any function can be approximated by a sum of orthogonal basis functions (such as power series and sine and cosine functions) multiplied by weighting factors (linear coefficients). For example, a power series expansion of a function f has the form:

$$f(x) \approx \sum_{i=0}^{i=n} c_i x^i \quad (3.12)$$

Since any two points lie on a line, and three lie in a plane, etc., a $n-1$ degree polynomial will pass through any given set of n points. However, the number of turns the polynomial makes increases with the degree, so interpolation between points with polynomial fitting functions could be dangerous.

Matching experimental data to mathematical functions is called *regression analysis* in statistics. Experimental data will have errors due to uncertainties in measurements. In this case we must settle on functions which pass as close as possible to the data, if not through them. A standard technique to optimize closeness minimizes the collective distance between the experimental points and the approximating curve. The collective distance may be expressed as the sum of the individual deviations between the points and the curve. Since distance is a difference which can be positive or negative, the absolute value of distance or square of distance is used to measure the deviation between the data and the curve. This prevents an artificial minimization of deviations due to cancellations of terms in the sum of distances.

The *linear least squares technique* for fitting functions to data assumes some finite linear expansion (sum) of individual (basis) functions as the approximating fitting function.

$$y(x) = \sum_{n=1}^{n=m} c_n f_n(x) \quad (3.13)$$

where the $f_n(x)$ are the given *basis functions* and the c_n are the linear coefficients, or *parameters* to be determined. The basis functions can take any form, including power, exponential, logarithm or trigonometric functions, and can include additional parameters. Finding the optimum values of the linear coefficient parameters c_n which minimize the deviation between the fitting function and the data is called *linear least squares analysis*. Finding the optimum values of the additional parameters requires a *non-linear least squares analysis*. The coefficients may be obtained using calculus to minimize the collective distance and linear algebra to solve the resulting set of simultaneous linear equations. We will not develop non-linear analysis here, but instead illustrate the process by treating the simplest polynomial case of $f_1 = 1$ and $f_2 = x$ (*linear regression*). For these basis functions, the coefficients are commonly symbolized by the letters b and m , and represent the intercept and slope, respectively, of the best-fit least-squares straight line. Given a set of n points $\{x_i, y_i\}$ to fit, the collective squared deviation D is

$$D(m, b) = \sum_{i=1}^{i=n} (mx_i + b - y_i)^2 \quad (3.14)$$

D is expressed as function of m and b because the object is to find the values of m and b which minimizes the deviation. The optimum values are:⁷

$$m = \frac{n \sum x_i y_i - \sum x_i \sum y_i}{n \sum (x_i)^2 - (\sum x_i)^2} \quad (3.15a)$$

$$b = \frac{\sum (x_i)^2 \sum y_i - \sum x_i \sum x_i y_i}{n \sum (x_i)^2 - (\sum x_i)^2} \quad (3.15b)$$

where the sums run from 1 to n . These formulas are often programmed into scientific and statistical pocket calculators with the contributing terms available for display by tapping selected keys.

⁷ For the mathematically intrepid, we offer the following derivation. Minima correspond to zero slopes, and slopes are represented as derivatives in calculus. Referring to Section 3.12 we see that minimizing the error is

Example 3.3 Find the best linear fit to the data $\{(1/273, \ln(0.0000472)), (1/298, \ln(0.00203)), (1/338, \ln(0.292))\}$.⁸

First, we will transform the set of three data points to a table of four-digit decimal values (compatible with an uncertainty of unity in the last place of the data):

x_i	y_i
0.003663	-9.961
0.003356	-6.200
0.002959	-1.231

Tabulating the terms of Eqns. (3.15a) and (3.15b) gives

$\sum x_i$	$\sum y_i$	$\sum (x_i)^2$	$\sum x_i y_i$
0.009978	-17.392	3.3436×10^{-5}	-0.060937

Applying Eqns. (3.15a) and (3.15b) to these data gives $m = -12400$ for the slope and $b = 35.45$ for the intercept.⁹

equivalent to setting the derivatives of E with respect to the parameters to zero:

$$\frac{\partial D(m, b)}{\partial m} = 0, \quad \frac{\partial D(m, b)}{\partial b} = 0$$

The ∂ symbol refers to “partial” differentiation with respect to one parameter at a time (slope in one direction). Applying a table of derivative formulas such as Table 3.1, these equations lead respectively to the algebraic equations

$$\begin{aligned} nb + (\sum x_i)m &= \sum y_i \\ (\sum x_i)b + (\sum x_i^2)m &= \sum x_i y_i \end{aligned}$$

where the sums run from 1 to n. These two linear algebraic equations in the unknowns b and m may be solved using the Linear Equation System Solving Algorithm of Section 3.9 to obtain the linear least squares formulas Eqs. (3.15).

⁸ This set of rather odd-looking values is actually the data of Example 18.5. In that example the slope $m = -E_a/R$, or $E_a = -Rm = -8.3145m$.

⁹ You should reproduce these calculations with your calculator. If it can do linear least squares regression, you can also check the final results directly.

Of course, it is always a good idea to plot the original data along with the regression equation to check that the fit looks reasonable. Section 3.12 describes how a regression analysis can be performed using computers.

Once an equation has been fit to the data, intermediate values may be easily determined (interpolation). Values outside the range of the data may be determined as well (extrapolation). Extrapolation is likely to be less reliable than interpolation, particularly for fitting curves with large curvature and/or “wiggles”, such as high-degree polynomials.

3.5. Solving Equations

Facility in setting up, rearranging and solving equations is basic to science. The setting up phase requires recognizing the problem to be one from which one (or more) equations can be derived in terms of known and unknown quantities. The equations are then *solved* for the desired variables by isolating the variables to one side of the equations according to equivalence-preserving operations. Because the names and symbols used for the variables may differ from the generic mathematical symbols, x , y , etc., some students experience difficulty making the connection between the chemistry and the math. It helps to recognize that *the rules of mathematics are independent of the symbols used*.

Algebraic *expressions* are collections of numbers and letters representing variables connected by *arithmetic operations*, addition, subtraction, multiplication, division and exponentiation. *Algebraic equations* connect two equivalent expressions with equals “signs” (= symbol). Collections connected only by addition, subtraction and equality are called *terms*. Algebraic expressions and equations involve functions of powers of variables. Ordinarily only linear (first power or “degree”) and quadratic (second power or “degree”) equations are encountered in beginning chemistry. Occasionally, higher degree or non-algebraic equations must be solved, so we include a numerical algorithm for their solution.

Manipulation of terms, expressions and equalities must preserve equivalence of value under arithmetic operations. Expression operations are usually used to simplify expressions. A list of basic operations which preserve expression equivalence is given below. A more complete list would include fraction and exponentiation equivalency operations as well.

Algebraic equivalence of expressions is preserved under the following operations:

1. Association under addition: $a + b = b + a$
2. Association under multiplication: $a \cdot b = b \cdot a$
3. Commutation under addition: $a + (b + c) = (a + b) + c$
4. Commutation under multiplication: $a \cdot (b \cdot c) = (a \cdot b) \cdot c$
5. Distribution under addition and multiplication: $a \cdot (b + c) = a \cdot b + a \cdot c$

Note that the inverse of the distribution operation is called *factoring*.

Equation operations are usually used to solve for (isolate) a variable. Equations may be manipulated by the following operations which preserve equivalence:

Algebraic equivalence of equations is preserved under the following operations:

1. Any expression equivalence operation.
2. Addition of the same value to both sides of the equation.
3. Subtraction of same value from both sides of the equation.
4. Multiplication by the same non-zero value into both sides of the equation.
5. Division by the same non-zero value into both sides of the equation.

A common rearrangement procedure based on these rules is *cross multiplication*. This algorithm rearranges an equality by transferring variables across the equals sign, from the numerator of one side to the denominator of the other.

Example 3.4 Solve the equation $4m = \frac{2r}{3}$ for r .

The 3 can be “cleared” from the denominator by multiplying both sides by 3, equivalent to transferring it across the equals sign to the numerator of the opposite side, as can the 2 in the numerator (by division), leaving the r by itself. The equation can be

reversed (using which operations?) and the fraction reduced to give

$$r = \frac{12m}{2} = \frac{2 \times 6 \times m}{2} = 6m.$$

3.6. Solving Linear Equations for One Variable

Lets develop a systematic algorithm for solving linear equations in one variable represented by x . If the equation can be cast into the form $ax + b = 0$, which we will call *standard linear form*, it can be solved for x by first subtracting the term represented by b from both sides to isolate the term in x , and then dividing both sides by the term represented by a to isolate x itself. Thus the algorithm consists of two parts, casting the equation into standard linear form and then solving the standard linear form. Casting into standard linear form in turn requires identification of the variable x , expression manipulations, and identification of the quantities a , b .

Linear Equation Solving Algorithm

Purpose: To solve a general linear equation in one variable, x .

Procedure:

Use the algebra equivalency operations to perform the following steps:

1. Rearrange the equation into the standard linear form $ax + b = 0$.
 - a) Identify the variable to be solved for as x .
 - b) Transfer all the terms onto the left side of the equation by subtracting any terms on the right side of the equation from both sides of the original equation, leaving 0 on the right side.
 - c) Collect all terms in x and its coefficients together using algebraic expression equivalence operations and identify the collected coefficient of x with the factor a .
 - d) Collect the remaining terms into a single term represented by b .
The equation is now in the standard linear form $ax + b = 0$.
2. Solve the standard linear form for the variable x to give the solution, $x = \frac{-b}{a}$.
 - a) Subtract the b term from both sides of the standard linear form.
 - b) Divide both sides by the a term.

Example 3.5 Solve the equation $C = \frac{5}{9}(F - 32)$ for F .

Since this equation is first degree (power) in F , we can follow the steps of the Linear Equation Solving Algorithm.

- 1a) Identify the variable to be solved for, x , with F .
- 1b) Transfer the term on the right side of the equation to the left side by subtraction, giving $C - \frac{5}{9}(F - 32) = 0$.
- 1c) There is only one term involving F , namely $-\frac{5}{9}(F - 32)$. Expanding this term (by

the distribution operation) produces two terms, $-\frac{5}{9}F + \frac{5}{9}(32)$. This identifies the factor a of F to be $-\frac{5}{9}$.

1d) Collecting the terms not involving F (by the addition association operation) identifies b as $C + \frac{5}{9}(32)$.

The equation is now in the form $aF + b = 0$.

2. Subtracting the term represented by b , dividing by the term represented by a , and

$$\text{simplifying gives } F = \frac{-b}{a} = \frac{-(C + \frac{5}{9}(32))}{-\frac{5}{9}} = \frac{9}{5}C + 32.$$

A few comments are in order. First, note that in this problem C is an independent variable, and that F is a variable dependent on the value of C . Steps 1c) and 1d) used expression equivalency operations, illustrating using a subalgorithm within an algorithm. The simplification of the final expression in step 2 assumes fraction and expression manipulations. Finally, the process is not necessarily the one an experienced algebraicist would use. For example, it would be more efficient to transfer the fraction $5/9$ to the left side as a first step. Although the algorithm may be not be clever, or may even be awkward, it is sure and general.

3.7. Solving Quadratic Equations for One Variable

If a second degree, or quadratic equation can be cast into the *standard quadratic form*, $ax^2 + bx + c = 0$, it can be solved for its two roots using a general formula, called the “quadratic formula”:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (3.16)$$

The algorithm for solving a quadratic equation is therefore similar to that for a linear equation, except for the final step.

Quadratic Equation Solving Algorithm

Purpose: To solve a general quadratic equation in one variable, x .

Procedure:

Use the algebra equivalency operations to perform the following steps:

1. Rearrange the equation into the standard quadratic form $ax^2 + bx + c = 0$.
 - a) Identify the variable to be solved for as x .
 - b) Transfer all the terms onto the left side of the equation by subtracting any terms on the right side of the equation from both sides of the original equation, leaving 0 on the right side.
 - c) Collect all terms in x^2 and its coefficients together using algebraic expression equivalence operations and identify the collected coefficient of x with the factor a .
 - d) Collect all terms in x and its coefficients together using algebraic expression equivalence operations and identify the collected coefficient of x with the factor b .
 - e) Collect the remaining terms into a single term represented by c .

The equation is now in the standard linear form $ax^2 + bx + c = 0$.

2. Use the quadratic formula to solve for the variable x in terms of the quantities identified by a , b and c : $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$.

3.8. Solving General Equations for One Variable

Algebraic equations of degree higher than four as well as many non-algebraic (or transcendental) equations have no “closed form” solution. However, *numerical approximations* to solutions can be obtained through several techniques. The idea is to find an algorithm which will get closer and closer to the solution by systematic repetition, or *iteration*.

We will start with a review of the linear and quadratic equations. Consider the graph of a general linear function $y(x) = mx + b$, where m represents the slope and b the y -intercept. The x -intercept of the graph represents the point at which $y(x) = 0$ (assuming real solutions exist), and can be related to the standard form of the linear equation $ax + b = 0$ by identifying m with a . A similar argument for quadratic functions identifies the two x -intercepts of the function as the two solutions to the standard quadratic form, $y(x) = ax^2 + bx + c = 0$. An x -intercept is called a *root* of the equation $y(x) = 0$, because it could be related to the square root of a number in the case of quadratic equations, the cube root for cubic equations, etc. Note that linear equations have one root, n th degree polynomial equations have n (possibly multiple, possibly imaginary) roots, and arbitrary equations involving powers and other (“transcendental”) functions terms may have many roots. In general then, *the real-valued solutions (or real roots) of an equation in one variable of the form $y(x) = 0$ occurs at the values of x (the roots) where the function $y(x)$ crosses the x -axis*. This property suggests algorithms for finding the solutions (real-valued roots) to general equations in one variable based on two steps, 1) casting the equation into the form $y(x) = 0$, and 2) locating the values (if any) of x where the function $y(x)$ crosses the x -axis. One possible way to locate the x -intercepts of $y(x) = 0$ would plot the graph of $y(x)$ and read where the function crosses the x -axis. This would be a *graphical* algorithm. More automated methods use calculators and computers.

How can a computer or calculator read a graph? Rather than giving it a graph as input, it can be given the equation of the graph, which is equivalent to the graph according to Descartes, as discussed above. (Tabular data could be used as well, but would require additional algorithms for interpolating intermediate points.) Actually, computers and calculators communicate through numbers (or symbols representing numbers), so the equation may be presented to a computer or calculator by giving it the parameters of the equation (a , b , c , etc. in the standard form equations above). If a way to represent searching for the x -intercept of the graph can be presented to the computer or calculator in terms of numbers as well, then the root finding process can be “automated” (calculated by the computer or calculator via an algorithm). Such methods are called *numerical methods*.

A guess at a value of x representing the root is improved in the graphical method by following the equation $y(x)$ to where it crosses the x -axis. An automated process for following the curve could take steps along the x -axis, computing the value of $y(x)$ at each step to decide the direction to take to bring $y(x)$ closer to 0. Three aspects of this automated process are

deciding how large a step to take, what to do when a root has been stepped over and when to stop. One method to address these aspects approximates the equation with a linear function coincident with the given function at one or more points (see Fig. 3.5). How far to step to the next approximation to a root may be determined by calculating where the linear function crosses the x-axis. A mathematical formula for deciding the next step can be obtained from the two-point form of linear equations, Eq. (3.10). The root of the two-point formula is at the value of x where y = 0. Solving Eq. (3.11) for x and setting y to 0 then provides a new guess to the root of the equation which the linear equation is approximating¹⁰:

$$x = x_1 - y_1 \left(\frac{x_2 - x_1}{y_2 - y_1} \right) \quad (3.17)$$

Continuous functions become straighter under magnification, no matter how curved. Thus the linear approximation to the equation to be solved becomes better as smaller pieces of the function near the place where the function crosses the x-axis are considered (i.e. near the root of the equation). The algorithm we have described is called the *secant method* in numerical analysis. If an initial guess to a root is sufficiently near the actual value, this process, when repeated (*iterated*) will *converge* to the value of the root. Convergence will be uniform for functions with positive curvature (concave downward) near the root (as in Fig. 3.5), but will be oscillatory for functions with negative curvature (concave upward) near the root.

¹⁰ If the function whose root is to be discovered has a known form, then the linear approximation to the slope may be replaced by the analytical derivative, $y' \equiv \frac{dy}{dx}$. This method, named for its inventor Isaac Newton, is less general but more rapidly convergent than the linear approximation. Given values of x, y and y' at one guess to the root, the next guess to the root is:

$$x = x_1 - y_1 / y'(x_1)$$

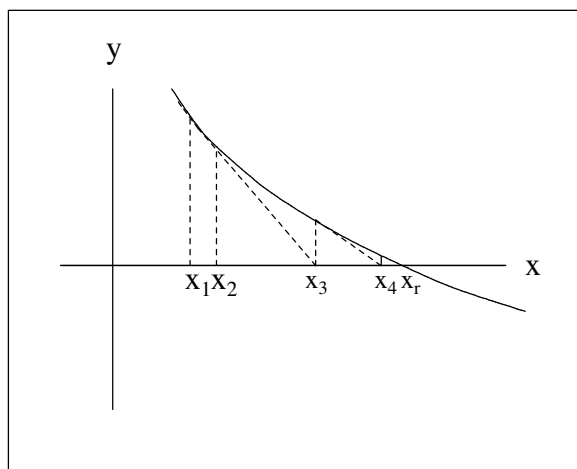


Fig. 3.5 Secant iteration to a root x_r where $y(x_r) = 0$.

Remaining decisions deal with checking to see the process isn't diverging (which can happen with poor initial guesses or where the function has zero slope), when to stop the process (either because the guess is sufficiently close to the root, or the process is diverging or cycling), and when to stop looking for more roots (some may be complex). These depend in part on the accuracy of the calculations and may not be easy to automate, although they may be easy to decide by a human observer, so we will give the basic algorithm and leave these details to refinements.

General One Variable Equation Solving Algorithm

Purpose: To solve for the roots of a general equation in one variable.

Procedure:

1. Use algebraic expression and equation equivalence operations to cast the given equation into the form $y(x) = 0$.
2. Choose two initial guesses x_1 and x_2 to the root x .
3. Evaluate the function for the values y_1 and y_2 at the values of x_1 and x_2 , respectively.
4. Compute a new guess x to the root from the linear approximation to the function:

$$x = x_1 - y_1 \left(\frac{x_2 - x_1}{y_2 - y_1} \right)$$

5. If $y(x)$ is not acceptably close to zero and is moving closer to zero (the process is converging), replace x_1 by x_2 and x_2 by x and repeat steps 3 and 4. If $y(x)$ is moving farther from zero, return to step 2 with a different set of initial guesses.

Example 3.6 Gases under limiting conditions of high temperature and low pressure obey an equation of state called the ideal gas law, $PV = nRT$, where P represents pressure in atm, V represents volume in liters, T represents temperature in Kelvin, n represents number of mols, and R is an universal constant equal to 0.0820578 in units consistent with those of the variables. The volume of one mol of ideal gas at a temperature of 273.150 K and pressure of 1 atm (“standard state”) has the value

$$V = \frac{nRT}{P} = \frac{(1)(0.0820578)(273.150)}{1} = 22.4141 \text{ liters} \quad (3.18)$$

Real gases obey more complicated state equations than the ideal gas law, such as the van der Waals equation of state:

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT, \quad (3.19)$$

where a and b are parameters (constants) characteristic of the gas. We would like to use the van der Waals equation of state to estimate the actual volume of one mol of carbon dioxide at standard temperature and pressure. For carbon dioxide, $a = 3.592$ and $b = 0.04267$ (in units consistent with the variables of the equation).

We want to solve the van der Waals equation for V , given values of P , T , n , a and b . Since the van der Waals equation is cubic in V (as can be seen by multiplying through by V^2), we are led to the General One Variable Equation Solving Algorithm.

1. Identify x with V and transfer all terms to the left hand side:

$$y(x) = \left(P + \frac{an^2}{x^2}\right)(x - nb) - RT = 0$$

Replacing the given variables and parameters with their values, $P = 1$, $T = 273.15$, $n = 1$, $a = 3.592$, $b = 0.04267$ yields

$$y(x) = \left(1 + \frac{3.592}{x^2}\right)(x - 0.04267) - 22.4141 = 0$$

2. Since we suspect that real gases are close to ideal gases, we can estimate the calculated volume to be close to 22.414 liters. We will arbitrarily choose for x_1 and x_2 the values 22.0 and 23.0, respectively.
3. From the values for x_1 and x_2 and the equation for $y(x)$ we obtain $y(x = 22.0) = -0.29381$ and $y(x = 23.0) = +0.69911$ (7 significant figures are justified in each term of the equation, but taking the difference of two near numbers reduces the number of significant figures to 5).
4. The new guess to $V = x$ is

$$x = x_1 - y_1 \left(\frac{x_2 - x_1}{y_2 - y_1} \right) = 22.0 - (-0.29381) \left(\frac{23.0 - 22.0}{(+0.69911) - (-0.29381)} \right) = 22.29591$$

(The 7 significant figures are regained in the addition.)

5. $y(x = 22.29591) = -6.5957 \times 10^{-5}$, which is closer to zero than both -0.29355 and $+0.69937$, suggesting convergence. Shifting x_1 to 23.0 and x_2 to 22.29591 gives $y_1(x = 23.0) = +0.69911$ and $y_2(x = 22.29591) = -6.5957 \times 10^{-5}$ and a new guess for $x = 22.29597$ with a corresponding $y(x) = -1.461 \times 10^{-8}$, which places y slightly closer to the x -axis intercept.

At this point the difference between the two guesses for V has dropped from -1.0 to 0.704 to -6.64×10^{-5} , and V has converged to the 5th place beyond the decimal, or the 7th significant figure. So the final result is $V = 22.29597$ liters for the molar volume of carbon dioxide at standard temperature and pressure (only $\frac{1}{2}\%$ away from the ideal value).

3.9. Solving Systems of Linear Equations for Several Variables

Solving for several variables simultaneously satisfying several equations can be quite complicated for general equations. Numerical methods such as the secant method may be extended to several variables. Instead of pursuing this, we will restrict ourselves to systems of *linear equations*, for which Karl Frederick Gauss found a straightforward deterministic (no iteration) algorithm, called the *method of elimination*.

Manipulating systems of equations requires additional equivalence operation rules for pairs of equations.

Algebraic equivalence of systems of equations is preserved under the following operations:

1. Interchange of the position of two equations in the system.
2. Addition of a constant multiple of one equation to another.

The second property includes subtraction of equations (which is addition of the negative of one equation to another).

The idea is to use the second operation to eliminate one variable between two equations. By doing this for all pairs of equations, the variable is left in just one equation. By repeating this procedure for the remaining equations, variables can be repeatedly eliminated in turn down to the last equation in the last variable. Then the value of the last variable is substituted into the next-to-last equation in two variables and solved for the second-to-last variable. This process of *back substitution* is repeated until values of all variables have been obtained. The steps are organized into the following algorithm for *consistent* sets of equations (n independent equations in n unknowns).

Linear Equation System Solving Algorithm

Purpose: To solve a system of linear equations with common variables for the variables.

Procedure:

1. Elimination process
 - a) Arrange all the equations using algebraic equation equivalence operations so that all the variables appear in the same order in each equation on the left hand side and remaining terms appear on the right hand side.
 - b) Choose one equation and apply the multiplication operation to convert the coefficient of the first variable to unity.
 - c) Eliminate the first variable in each equation succeeding the first equation by multiplying the first equation by the value of the coefficient of the first variable in each succeeding equation and subtracting the resulting equation from each succeeding equation.
 - d) As long as enough equations remain (the system remains *consistent*), move down one equation and repeat steps 1b) and 1c) to eliminate succeeding variables, until all but the last variable is eliminated in the last equation.
2. Back substitution process
 - a) Solve the last equation for the value of the last variable.
 - b) Substitute the value of the last variable into the second-to-last equation, and solve for the value of the second-to-last variable.
 - c) Repeat steps 2b) and 2c) working up to the original first equation.

Example 3.7 Solve the system:

$$\begin{aligned}x + y + z &= 6 \\2x - y + z &= 3\end{aligned}$$

$$x + 2y - 3z = -4$$

Steps 1a) and 1b) are already done. Eliminating x in the second and third equations according to step 1c) gives (by multiplying the first equation by 2 and subtracting from the second, the multiplying the first equation by 1 and subtracting from the third)

$$\begin{aligned} x + y + z &= 6 \\ -3y - z &= -9 \\ y - 4z &= -10 \end{aligned}$$

Starting at the second equation and choosing to eliminate the second variable, y by repetition of step 1b) gives:

$$\begin{aligned} x + y + z &= 6 \\ y + \frac{z}{3} &= 3 \\ y - 4z &= -10 \end{aligned}$$

Repeating step 1c) starting at the second equation gives:

$$\begin{aligned} x + y + z &= 6 \\ y + \frac{z}{3} &= 3 \\ -\frac{13}{3}z &= -13 \end{aligned}$$

We have arrived at the last equation. Working back up according to step 2 and solving for z , then y , then x gives:

$$\begin{aligned} z &= 3 \\ y &= 2 \\ x &= 1 \end{aligned}$$

Section 3.12 shows how a system of linear equations can be solved using computers.

3.10. Geometry

Geometry (Gr. *gaia* = earth + *metrein* = measure) is the formal science of the shapes of objects. As its name suggests, geometry has its roots in the practical determination of land property, but of course is applicable to any object. It is an independent mathematical system but uses the tools of algebra for manipulating information.

The principle geometry application in introductory chemistry is for analyzing molecular shapes and packing. This will be explained in the proper place, but for now we will summarize a few facts.

Physical objects exist in three-dimensional space. A box (cube) in space has sides (edges) of equal length. One of the most famous numbers in mathematics is the length of the diagonal of the face of a cube expressed in terms of the length of the edges. The three lengths are related through the famous theorem of Pythagoras which says that the sum of the squares of the lengths of the edges (e) adjacent to a right (90 degree) angle in a triangle (the legs) is equal to the square of the length (h) of the third side (the *hypotenuse*). Solving

$$e^2 + e^2 = h^2$$

algebraically for h leads to

$$h = \sqrt{2}e \quad (3.20)$$

The number $\sqrt{2}$ is of interest because it is an “*irrational*” number, that is a number which cannot be expressed as a fraction with integers (rational number). Expressed as a decimal, it is a never-ending number. Pi and e are further examples of irrational numbers. The length of the diagonal of the cube (from one corner, or apex to the opposite corner) can be found by a couple of applications of Pythagoras’ theorem to be $\sqrt{3}e$. Fig. 3.6 summarizes this relationship.

¹⁰ Can you guess the length of the diagonal of a *tesseract* (four-dimensional cube)?

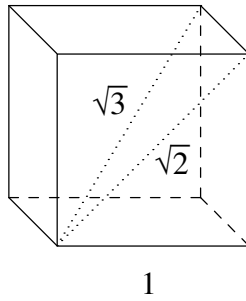


Fig. 3.6 Diagonals of the Cube

Trigonometry (Gr. *trigonon* = triangle + *metrein* = measure) is concerned with the relationships between the angles and edges of closed three-sided geometric figures called triangles and more generally, polygons (many-sided figures). Angles are commonly measured in units of *radians* or *degrees*. For example, the sum of the angles of a triangle lying in a plane is 2π radians, or 360° , the total angle a line sweeps in rotating about a point on the line back to its original position. Edges and angles in triangles are related to each other through *trigonometric functions*. Three fundamental “trig” functions are the *sine*, *cosine* (*cos*) and *tangent* (*tan*), defined as the ratios of the lengths of the adjacent over the hypotenuse sides, the opposite over the hypotenuse sides, and the opposite over the adjacent sides, respectively, of an angle in a right triangle. A basic property of trig functions which can be derived from the Pythagorean theorem is that

$$\sin^2(\theta) + \cos^2(\theta) = 1 \tag{3.21}$$

where $\sin^2(\theta)$ stands for the square of the sine of any angle theta (θ). Another basic relation is Euler’s identity:

$$\exp ix = \cos(x) + i \sin(x) \tag{3.22}$$

For the special case $x = \pi$, Euler’s identity relates a number of interesting fundamental mathematical quantities:

$$e^{i\pi} = -1. \tag{3.23}$$

Trig functions are readily available on scientific calculators.

Additional geometric figures besides triangles and cubes that are of interest to chemists include “regular” (equal sided) polyhedra (many faces), such as the *tetrahedron*, which can be inscribed in a cube by connecting alternating vertices. A little work with geometry and trigonometry shows that the angle between two lines from the center of a tetrahedron to two different vertices is approximately 109.5° . Fig. 3.7 illustrates these relationships.

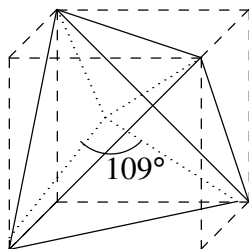


Fig. 3.7 The Tetrahedron Inscribed in a Cube

3.11. Calculus

Although ability with calculus is traditionally not expected in lower-level introductory chemistry classes, most students nowadays have taken a calculus course before they take chemistry. Some results in chemistry rely on calculus, without which it is difficult to discuss them.

Elementary *Calculus* (L. *calcularre* = to calculate) is concerned with the slopes, or “derivatives” of curves (*differential calculus*), and the areas or “integrals” under curves (*integral calculus*). Derivatives and integrals mathematically are functions, called *operators*, which produce new functions from given functions. Special symbols are used to represent calculus operators of a function $f(x)$, $\frac{df(x)}{dx}$ for derivatives and $\int f(x)$ for integrals.

Definite derivatives and integrals are numerical values of derivatives and integrals evaluated at given points (point on a curve for the derivative slope, and end points of a curve for

integral areas). The derivative of a function and its integral are *inverse* functions of each other, that is, one “undoes” what the other does (like square and square root operations). Derivatives of derivatives (higher order derivatives) are symbolized as $\frac{df^n(x)}{dx^n} \equiv \frac{d}{dx} \left(\frac{d}{dx} \left(\dots \frac{df}{dx} \dots \right) \right)$ for *order* $n = 2$ (second), etc, and represent geometric curvature, etc.¹¹

Obtaining the derivative or integral of an arbitrary function may require numerical approximation (approximate results through numerical techniques). Graphically, derivatives can be approximated as tangents to curves, and integrals as the sum of little contiguous pieces, such as squares or rectangles. Pocket scientific calculators sometimes provide some calculus capability, while larger computers use “symbolic computation” to produce calculus functions. Derivatives and integrals of certain “analytic” functions are tabulated, a few of which are given in Table 3.1. More extensive tables are found in various handbooks.

¹¹ Nested functions are called *iterated* functions.

Table 3.1 Analytic Derivatives and Integrals (a is a parameter)

Function $f(x)$	Derivative $\frac{df(x)}{dx}$	Integral $\int f(x)$
a	0	ax
x^n	nx^{n-1}	$\begin{cases} \frac{x^{n+1}}{n+1} & n \neq -1 \\ \ln(x) & n = -1 \end{cases}$
e^{ax}	ae^{ax}	$\frac{e^{ax}}{a}$
$\sin(ax)$	$a \cos(ax)$	$\frac{-\cos(ax)}{a}$
$\cos(ax)$	$-a \sin(x)$	$\frac{\sin(ax)}{a}$

The evaluation of derivatives of expressions uses rules such as the derivative or integral of a sum of functions $f(x)+g(x)$ is the sum of the derivatives or integrals: $\frac{d(f+g)}{dx} = \frac{df}{dx} + \frac{dg}{dx}$, the derivative of a product of functions $f(x)g(x)$ is the sum of the first times the derivative of the second plus the second times the derivative of the first: $\frac{d(fg)}{dx} = f \frac{dg}{dx} + g \frac{df}{dx}$, and the derivative with respect to one variable of a function of a second variable is the product of the derivative of the function with respect to its variable and the derivative of the a second variable with respect to the first: $\frac{df(y)}{dx} = \frac{df(y)}{dy} \frac{dy}{dx}$ (the “composite” or “chain” rule).

Multivariate calculus extends the geometric notions of tangent slope, curvature and area to gradients (directional derivatives), curvature and volume in multiple dimensions. For example, the gradient of a scalar (non-vector) function $f(x,y,z)$ in three-dimensional Cartesian coordinate space is a vector with three components, given by

$$\nabla f = \frac{\partial f}{\partial x} \vec{i} + \frac{\partial f}{\partial y} \vec{j} + \frac{\partial f}{\partial z} \vec{k} \quad (3.24)$$

and the curvature is given by

$$\nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \quad (3.25)$$

The ∂ symbol refers to *partial differentiation* or differentiation with respect to one variable considering any others to be constant. ∇ (pronounced “del”) is called the *Laplacian operator* in honor of the Eighteenth Century mathematician Pierre Simon Le marquis de Laplace. Application of ∇ to a vector function $\vec{f}(x, y, z) = f_1 \vec{i} + f_2 \vec{j} + f_3 \vec{k}$ in three-dimensional Cartesian coordinate space is a scalar, called the *divergence*:

$$\nabla \cdot \vec{f} = \frac{\partial f_1}{\partial x} + \frac{\partial f_2}{\partial y} + \frac{\partial f_3}{\partial z} \quad (3.26)$$

Section 3.12 shows how calculus expressions can be evaluated using computers.

3.12. Computer Mathematics

Computers can be instructed (*programmed*) to perform a variety of mathematical processes. Programs are written in *languages* understandable to both humans and computers. The symbols (*alphabet*), terms (*words*), meaning (*syntax*) and rules (*grammar*) of programming languages resemble human communication languages, but are very precisely defined. Program instructions must accurately obey the rules of the language to be understandable (translatable) by computers.

A variety of computer languages have been designed to facilitate the process of telling the computer how to manipulate information fed in (*input*) to produce new information (results, called *output*). The simplest programming languages perform arithmetic on (integer and real) numbers. The symbols (alphabet) of the simplest of these languages consist of digits, decimal point, and arithmetic operations of addition, subtraction, multiplication, division and expression evaluation. Extensions might include symbols to represent powers (for computing powers and for scientific notation representation of reals), integer factorials and integer remainders (modulus). Expressions consist of sequences (*strings*) of digits (with possible decimal point) and operations constructed according to the rules of arithmetic. The simplest arithmetic pocket calculators are programmed to accept input through keys to evaluate arithmetic expressions as sequences of numbers and operations.

More sophisticated languages and programs implement algorithms to manipulate variables representing numbers to perform more general mathematical operations. “Scientific”, “programmable” and “graphing” calculators exhibit a range of such capabilities. Higher-level languages and programs approach human communication and thinking to perform symbolic mathematics. We will illustrate the use of a sophisticated package of programs called MAPLE¹² to rework some of the examples of this chapter. Input statements follow the `>` prompt and end with a semicolon (`;`) (which causes action to occur and output to be displayed) or colon (`:`) (no output displayed). The statements are processed by the program as soon as they are entered and results displayed (*interactive* mode). Comments (which are useful to humans but not processed by the computer) begin with `#`. The symbol `:=` is like a definition and causes the expression on the right side of `:=` to be identified with, or *assigned* to the variable on the left side. The braces `{}` and brackets `[]` symbolize (unordered) sets and (ordered) lists (called *arrays*), respectively, with members separated by commas. Note that lists can be nested into lists of lists (n-dimensional *matrices*). Arithmetic operations include `+`, `-`, `*`, `/`, `^`, `Float`, representing addition, subtraction, multiplication, division, power and real scientific number notation, respectively. Transcendental functions are recognized (`sin`, `cos`, `ln`, etc). Many mathematical operations are permitted, such as `solve` which signals the program to attempt to solve a set of equations for a set of variables, and `diff` and `int` for differentiation and integration. Further information can be found by entering `?` at the MAPLE prompt `>`.

A handy feature of MAPLE is the ability to read commands from a file external to MAPLE (you can see the manual by entering `?read;` inside MAPLE). Creating a file requires a *text editor*. There are many text editors. We will describe one that is standard on UNIX operating systems, called *vi* (for *visual interactive*). The *Unix Vi* editor may be used to create and edit text files (files containing characters that appear on computer keyboards.) *Vi* is a sophisticated editor with a great many features, but a few simple operations suffice to do most editing tasks. Basically one has four editing needs: invoke the editor, enter new text (characters from a keyboard), modify existing text, and exit the editor.

To create a new file or edit an existing file, one enters `vi filename [ENTER]`, where *filename* is the name of the file to be created or modified. To save the current contents of the

¹² Copyright © 1981-1990 by the University of Waterloo. MAPLE is a registered trademark of Waterloo Maple Software.

file produced by *vi*, press in sequence the keys `:w [ENTER]` (for write); to exit the *vi* editor, press the keys `:q [ENTER]` (for quit). New text can be entered by pressing the `i` key (for insert) and typing in the text to be inserted until the ESC key is pressed.¹³

Changes to a file are made by moving the position cursor displayed on the screen to the place where the change is to be made and then deleting and/or inserting text. Pressing the `H`, `J`, `K`, `L` (“arrow”) keys will move the cursor in *vi* to the left, down, up or right, respectively. A string of text characters can be located by entering `/string [ENTER]` (forward slash followed with the string to be searched for). A character can be deleted by pressing the `x` key (“x-ed” out); n characters can be deleted by pressing `nx`, where n represents a digit key. Pressing `ndw` deletes n words and pressing `ndd` deletes n lines.

A very useful feature in *vi* is the `u` (or `U` key), which will undo the last change made (or all the changes made on the current line). Repeating `u` (or `U`) will toggle the effect. Many UNIX systems have a *vi* tutorial which can be invoked by entering `learn vi` at the UNIX input prompt.

Let’s rework some of the examples of this chapter using MAPLE. Here is the input and output from an interactive MAPLE session on a typical computer:

```
# Example 3.5

# DEFINE A LINEAR EQUATION
> eqn:=C = (5/9)*(F-32);

                               eqn := C = 5/9 F - 160/9

# SOLVE THE LINEAR EQUATION
> F:=solve(eqn,F);

                               F := 9/5 C + 32
```

¹³ The most common mistake using the *vi* editor is forgetting to press the ESC key to finish inserting text!

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```
# Example 3.7

# DEFINE A SYSTEM OF LINEAR EQUATIONS
> eqn1:=x+y+z=6;
                                eqn1 := x + y + z = 6

> eqn2:=2*x-y+z=3;
                                eqn2 := 2 x - y + z = 3

> eqn3:=x+2*y-3*z=-4;
                                eqn3 := x + 2 y - 3 z = -4

# SOLVE THE SYSTEM
> solve({eqn1,eqn2,eqn3},{x,y,z});
                                {x = 1, z = 3, y = 2}

# Example 3.6

# DEFINE PARAMETER VALUES
> R:=0.0820578;
                                R := .0820578

> a:=3.592;
                                a := 3.592

> b:=0.04267;
                                b := .04267

# DEFINE STATE VARIABLE VALUES
> n:=1;
                                n := 1
```

```

> P:=1;
                                     P := 1

> T:=273.15;
                                     T := 273.15

# DEFINE THE EQUATION OF STATE
> vdW:=(P+(a*n^2)/V^2)*(V-n*b)=R*T;

                                     / 3.592\
vdW := |1 + -----| (V - .04267) = 22.41408807
                                     | 2 |
                                     \ V /

# SOLVE THE EQUATION OF STATE FOR V
> V:=solve(vdW,V);
V := 22.29596099, .080398545 + .02025936702 I, .080398545 - .02025936702 I

# EXIT
> quit;

```

Note in Example 3.6 that the equation to be solved is a cubic polynomial equation. Therefore three solutions (values of volume V) are expected, but (fortunately) only one is a real value as imaginary volume is unphysical. This illustrates the difference between strictly mathematical models and physical situations.

The next example performs regression analysis and requires loading in the `stats` library of operations. Here is the contents of the input file to MAPLE:

```
# INPUT DATA
```

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```
data:=[1/273,ln(Float(4.72,-5))], [1/298,ln(0.00203)], [1/338,ln(.292)]; # Input

# FIT DATA
statdat:=array([[x,y],data]); # Augment data with variables
parameters:=stats[regression](statdat, y=m*x+b); # Find best fit parameters
assign(parameters): # Assign values to parameters

# PLOT DATA AND FIT
plot({[data],m*x+b},x=data[1][1]..data[3][1]); # Terminal plot

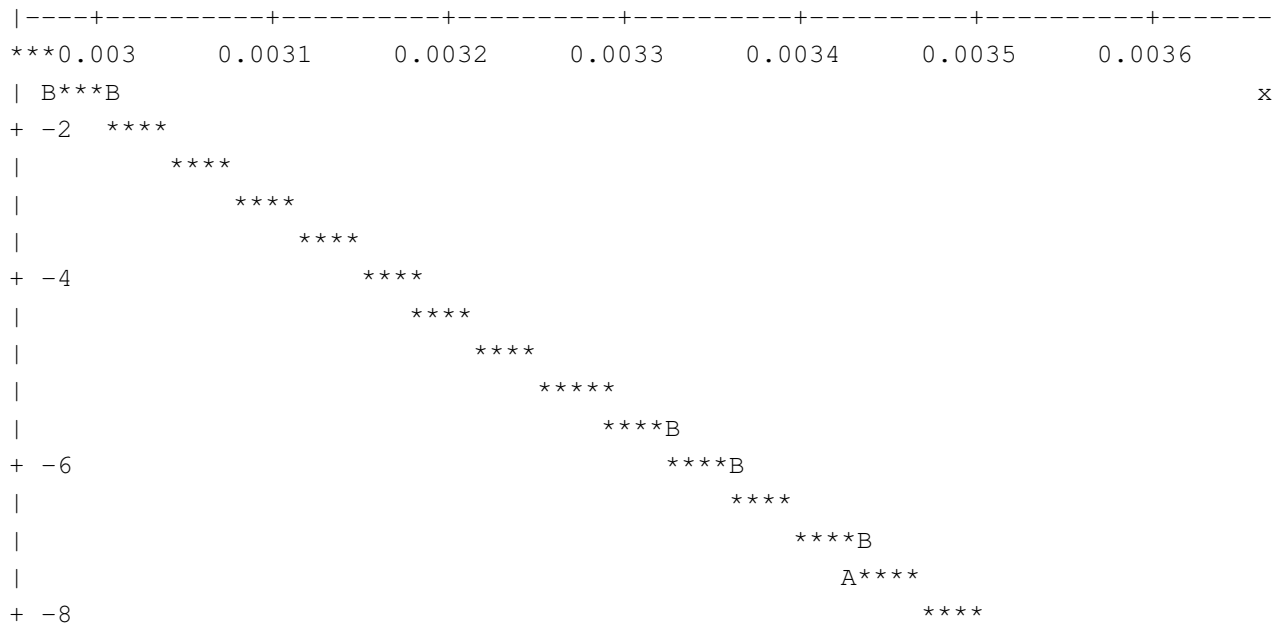
# EXIT
quit;
```

And here is the corresponding output:

```
data :=
    [1/273, ln(Float(4.72, -5))], [1/298, -6.199719486], [1/338, -1.231001477]

    [ x          y          ]
    [           ]
    [ 1/273  ln(Float(4.72, -5)) ]
statdat := [           ]
    [ 1/298      -6.199719486   ]
    [           ]
    [ 1/338      -1.231001477   ]

parameters := {m = -12398.91807, b = 35.43858063}
```





The fitting curve passes close to the data points, supporting a linear fit of the data.

A comparison of the computer method with hand methods should convince one of the advantages to using computers to solve mathematical problems.

Summary

Chemistry is a physical science that uses principles and processes from physics and mathematics. Mathematical equations contain quantities which represent experimental variables and parameters characteristic of the system being described.

Simple physical models have simple mathematical representations. Each mathematical equation has an equivalent graph, so equations can be solved algebraically, graphically, or numerically. Computers may be programmed to automate mathematical manipulations.

MATHEMATICAL TOOLS EXERCISES

1. What is the sum of the first 100 integers?
2. How many different ways can ten people be seated (arranged) at a table.
3. Calculate the value of e to the tenth decimal place.
4. What is the slope of a straight line passing through the points (0,1) and (1,0)?
5. What is the slope of the curve $y = x^2$ at the origin, and at the point where x has the value 1?
6. What is the value of 4 divided by $\frac{1}{2}$?
7. Evaluate the slope of the $\ln(p)$ vs. $1/T$ butane vapor pressure data of Table 14.1.
8. Repeat the molar volume of carbon dioxide calculation of the example of the text using 22.0 and 22.4 as the starting guesses.
9. If you have access to a symbolic mathematic computer program, use it to solve the system of linear equations associated with balancing the chemical reaction of Example 11.2.

MATHEMATICAL TOOLS EXERCISE HINTS

1. Don't do this by addition.
2. Ten ways for the first person, nine for the second, ... one for the last.
3. Evaluate enough terms in the expansion of $\exp x$ for $x = 1$. (No fair using the e^x key on a calculator.)
4. Refer the Algorithm for Determining the Slope of a Curve.
5. It may help to plot the function.

6. Use algebraic equivalence operations.
7. Refer to Example 3.3 and the MAPLE examples in Section 3.12.
8. Follow Example 3.6 and the MAPLE examples in Section 3.12.
9. You don't have to understand any chemistry to solve this problem. Just scan the example to locate the system of linear equations.