Silbey, Alberty & Bawendi, "Physical Chemistry" 4th Ed.

D Mathematical Relations

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D.1 LOGARITHMS AND EXPONENTIALS

The natural logarithm of a number x is the power to which e = 2.718281 ... must be raised to yield x. This definition and the properties of natural logarithms are summarized by

$$\begin{aligned} e^{\ln x} &= x \\ \ln(xy) &= \ln x + \ln y \\ \ln(x/y) &= \ln x - \ln y \\ \ln x^{y} &= y \ln x \end{aligned}$$

The base 10 logarithm of a number x is the power to which 10 must be raised to yield x.

$$\begin{aligned} 10^{\log x} &= x \\ \ln x &= \ln(10) \log x = 2.303 \log x \end{aligned}$$

Exponential functions have the following properties:

$$a^{m+n} = a^m a^n$$
$$a^m/a^n = a^{m-n}$$
$$(a^m)^n = a^{mn}$$

D.2 SERIES

It is often of interest to see the form of an equation when one of the quantities becomes indefinitely small or indefinitely large. Since most functions we deal with can be expressed by infinite series, the series expression can be used with higher-order terms omitted. The series expression for a function f can be calculated with the Maclaurin series:

$$f(x) = f(0) + \left(\frac{\mathrm{d}f}{\mathrm{d}x}\right)_{x=0} x + \frac{1}{2!}\left(\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\right)_{x=0} x^2 + \cdots$$

The following infinite series are examples of Maclaurin series:

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} + \cdots \qquad [\text{all } x]$$
$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \cdots \qquad [\text{all } x]$$
$$\mathrm{e}^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots \qquad [\text{all } x]$$
$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots \qquad [x^2 < 1]$$
$$(1+x)^{-1} = 1 - x + x^2 - x^3 + \cdots \qquad [x^2 < 1]$$
$$(1-x)^{-1} = 1 + x + x^2 + x^3 + \cdots \qquad [x^2 < 1]$$
$$(1-x)^{-2} = 1 + 2x + 3x^2 + 4x^3 + \cdots \qquad [x^2 < 1]$$
$$(1+x)^{1/2} = 1 + \frac{x}{2} - \frac{x^2}{8} + \frac{x^3}{16} - \cdots \qquad [x^2 < 1]$$

The series $(1 + x)^n$ is referred to as the binomial series. If n is an integer, the series terminates after $(n + 1)$ terms, but when n is not an integer, the series is infinite:

$$(1+x)^n = 1 + nx + \frac{n(n-1)}{2!}x^2 + \frac{n(n-1)(n-2)}{3!}x^3 + \cdots \qquad [x^2 < 1]$$

A Maclaurin series is an expansion about the point $x = 0$. A Taylor series is an expansion about $x = x_0$. The Taylor series is

$$f(x) = f(x = x_0) + \left(\frac{\mathrm{d}f}{\mathrm{d}x}\right)_{x_0} (x - x_0) + \frac{1}{2!}\left(\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\right)_{x_0} (x - x_0)^2 + \cdots$$

D.3 CALCULUS

Some basic derivatives are

$$\frac{du^n}{dx} = nu^{n-1}\frac{du}{dx}$$

$$\frac{d\,e^u}{dx} = e^u\frac{du}{dx}$$

$$\frac{d\ln x}{dx} = \frac{1}{x}$$

$$\frac{d\sin x}{dx} = \cos x$$

$$\frac{d\cos x}{dx} = -\sin x$$

$$\frac{dz[y(x)]}{dx} = \frac{dz}{dy}\frac{dy}{dx} \qquad \text{(chain rule)}$$

$$\frac{d(u+v)}{dx} = \frac{du}{dx} + \frac{dv}{dx}$$

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1 \qquad \text{(cyclic rule)}$$

$$\frac{d(uv)}{dx} = u\frac{dv}{dx} + v\frac{du}{dx}$$

$$\frac{d(u/v)}{dx} = \frac{v(du/dx) - u(dv/dx)}{v^2}$$

Some basic indefinite integrals are

$$\int x^\alpha dx = \frac{1}{\alpha+1}x^{\alpha+1} \qquad (\alpha \neq -1)$$

$$\int e^{ax} dx = \frac{1}{a} e^{ax}$$

$$\int \frac{dx}{x} = \ln|x|$$

$$\int \ln ax \, dx = x \ln ax - x$$

$$\int x^2 e^{bx} dx = e^{bx}\left(\frac{x^2}{b} - \frac{2x}{b^2} + \frac{2}{b^3}\right)$$

Some basic definite integrals are

$$\int_0^\infty e^{-ax}\, dx = \frac{1}{a}$$

$$\int_0^\infty x^n e^{-qx}\, dx = \frac{n!}{q^{n+1}} \qquad (n > -1, q > 0)$$

$$\int_0^\infty e^{-bx^2}\,dx = \frac{1}{2}\left(\frac{\pi}{b}\right)^{1/2}$$

$$\int_0^\infty x^{2n}e^{-bx^2}\,dx = \frac{1\cdot 3\cdots(2n-1)}{2^{n+1}}\left(\frac{\pi}{b^{2n+1}}\right)^{1/2} \qquad (n = 1, 2, 3, \ldots)$$

$$\int_t^\infty z^n e^{-az}\,dz = \frac{n!}{a^{n+1}}e^{-at}\left(1 + at + \frac{a^2t^2}{2!} + \cdots + \frac{a^nt^n}{n!}\right) \qquad (n = 0, 1, 2, \ldots)$$

$$\int_0^{\pi/2} \sin^2 nx\,dx = \int_0^{\pi/2} \cos^2 nx\,dx = \frac{\pi}{4} \qquad (n = 1, 2, 3, \ldots)$$

$$\int_0^{2\pi} \sin mx \sin nx\,dx = \int_0^{2\pi} \cos mx \cos nx\,dx = 0 \qquad (m \neq n)$$

Also see Table 17.1 for definite integrals.

D.4 SPHERICAL COORDINATES

The choice of a coordinate system is a matter of convenience. When a system has some kind of a natural center, as in the case of an atom, spherical coordinates are convenient, as indicated by Fig. D.4.1. The angle θ is the declination from the north pole, so $0 \leq \theta \leq \pi$. Since there is not a natural zero value for ϕ, the angle around the equator is measured from the x axis, as indicated in the figure, and $0 \leq \phi \leq 2\pi$. Since r is the distance from the origin, $0 \leq r \leq \infty$.

The Cartesian coordinates x, y, and z are related to the spherical coordinates r, θ, and ϕ by

$$x = r \sin\theta \cos\phi \qquad \text{(D.4.1)}$$

$$y = r \sin\theta \sin\phi \qquad \text{(D.4.2)}$$

$$z = r \cos\theta \qquad \text{(D.4.3)}$$

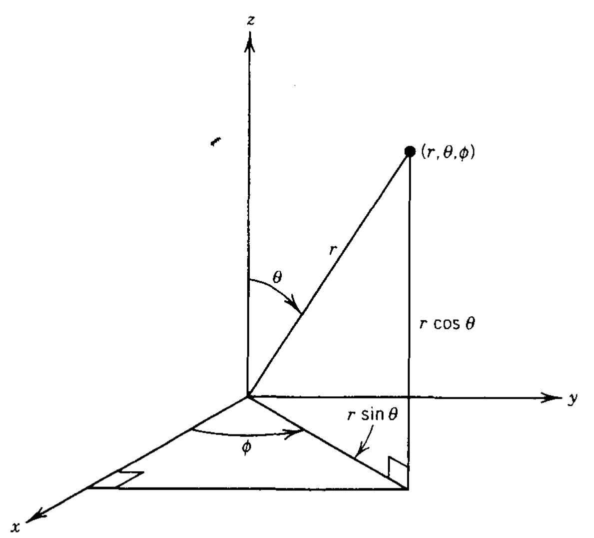

Figure D.4.1 Spherical coordinate system where a point is specified by r, θ, and ϕ.

It is readily shown that the spherical coordinates are related to the Cartesian coordinates by

$$r = (x^2 + y^2 + z^2)^{1/2} \tag{D.4.4}$$

$$\cos\theta = \frac{z}{(x^2 + y^2 + z^2)^{1/2}} \tag{D.4.5}$$

$$\tan\phi = \frac{y}{x} \tag{D.4.6}$$

Figure D.4.2 shows that the differential volume element in spherical coordinates is

$$\mathrm{d}V = (r \sin\theta\, \mathrm{d}\phi)\,(r\, \mathrm{d}\theta)\, \mathrm{d}r = r^2 \sin\theta\, \mathrm{d}r\, \mathrm{d}\theta\, \mathrm{d}\phi \tag{D.4.7}$$

It also shows that in spherical coordinates the differential area is given by

$$\mathrm{d}A = r^2 \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi \tag{D.4.8}$$

The volume of a sphere of radius a is given by

$$V = \int_0^a r^2\, \mathrm{d}r \int_0^\pi \sin\theta\, \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi = \left(\frac{a^3}{3}\right)(2)(2\pi) = \frac{4\pi a^3}{3} \tag{D.4.9}$$

The surface area of a sphere of radius a is given by

$$A = a^2 \int_0^\pi \sin\theta\, \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi = a^2(2)(2\pi) = 4\pi r^2 \tag{D.4.10}$$

We can integrate a function $f(r, \theta, \phi)$ over the full range of these coordinates by use of

$$F = \int_0^\infty r^2\, \mathrm{d}r \int_0^\pi \sin\theta\, \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi\, f(r, \theta, \phi) \tag{D.4.11}$$

An example of this type of integral is the orthogonality relation of atomic wavefunctions.

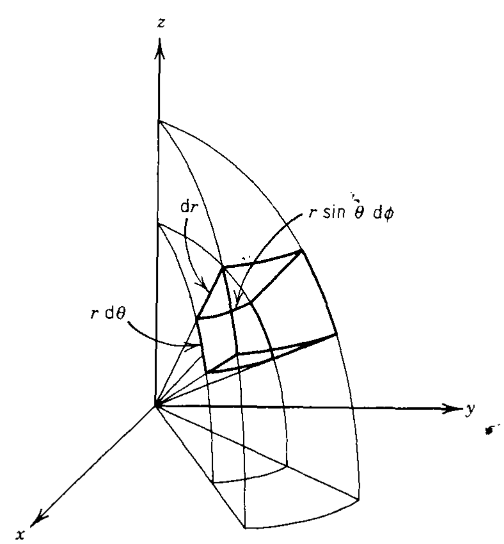

Figure D.4.2 Volume element in a spherical coordinate system.

D.5 LEGENDRE TRANSFORMS

The variables in a function can be changed by simply substituting an expression for a variable in terms of a new variable. For example, the thermodynamic temperature T in an equation can be replaced using $T = t + 273.15$ to obtain the equation written in terms of the Celsius temperature t. Another way to change variables involves defining a new property that depends on a derivative of the original function, rather than a new variable such as t in this example. This method, which is especially useful in thermodynamics, is referred to as a **Legendre transform.**

Consider a function $f(x)$ that is differentiable for all x; this function is plotted in Fig. D.5.1. The total differential of f is given by

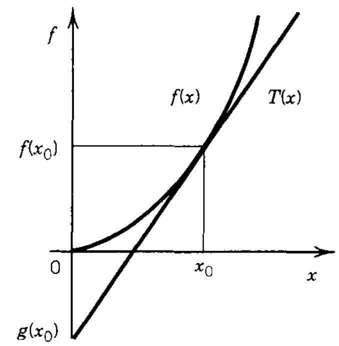

Figure D.5.1 Plot of $f(x)$ versus x.

$$df = \frac{df}{dx}dx = p(x)\,dx \qquad (D.5.1)$$

where the function $p(x)$ is the slope $f'(x)$ of $f(x)$ at every value of x. The objective of the Legendre transform is to find a function $g(p)$ of the new variable $p = f'(x)$ that is equivalent to $f(x)$. By equivalent we mean that $f(x)$ and $g(p)$ contain the same information; in short, $g(p)$ can be calculated from $f(x)$, and $f(x)$ can be calculated from $g(p)$. The new function $g(p)$ can be obtained by use of Fig. D.5.1. The value of p at any point along $f(x)$ is the slope $f'(x)$. It is evident from the figure that the equation for the tangent $T(x)$ at any point x_0 along the curve is

$$T(x) = f(x_0) + f'(x_0)(x - x_0) \qquad (D.5.2)$$

The intersection of the tangent with the vertical axis is given by

$$g(x_0) = f(x_0) - x_0 f'(x_0) \qquad (D.5.3)$$

The value of function g depends on x_0 and, for a general x_0,

$$g = f - xf'(x) = f - xp \qquad (D.5.4)$$

The new function g is referred to as the Legendre transform of f, and this equation shows that g is obtained from f by subtracting xp, which is $xf'(x)$. This process can be generalized to functions of two or more variables.

In Chapter 4 we found that the internal energy U is a function of S and V. However, S and V may not be experimentally convenient variables. The following Legendre transform was used to define the Gibbs energy G:

$$G = U + PV - TS = U - V\left(\frac{\partial U}{\partial V}\right)_S - S\left(\frac{\partial U}{\partial S}\right)_V \qquad (D.5.5)$$

As shown in Chapter 4, the Gibbs energy is a function of T and P, which are convenient independent variables for work in the laboratory.

D.6 DETERMINANTS

A determinant is a square array of numbers. Its value is defined as a certain sum of products of subsets of the elements. If the determinant has n rows and columns, each term in the sum will have n factors in it. For a determinant of order 2,

$$\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix} = a_1 b_2 - a_2 b_1$$

The value of a large determinant may be obtained by expanding by minors. For a determinant of order 3,

$$\begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix} = a_1 \begin{vmatrix} b_2 & c_2 \\ b_3 & c_3 \end{vmatrix} - b_1 \begin{vmatrix} a_2 & c_2 \\ a_3 & c_3 \end{vmatrix} + c_1 \begin{vmatrix} a_2 & b_2 \\ a_3 & b_3 \end{vmatrix}$$

$$= a_1b_2c_3 + a_2b_3c_1 + a_3b_1c_2 - a_3b_2c_1 - a_2b_1c_3 - a_1b_3c_2$$

Determinants of higher order are defined by an analogous row (or column) expansion.

Simultaneous linear equations can be solved using determinants. For example, consider the set

$$a_{11}x + a_{12}y + a_{13}z = c_1$$
$$a_{21}x + a_{22}y + a_{23}z = c_2$$
$$a_{31}x + a_{32}y + a_{33}z = c_3$$

The determinant of the coefficients of x, y, and z is

$$D = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}$$

It can be shown that

$$x = \frac{1}{D} \begin{vmatrix} c_1 & a_{12} & a_{13} \\ c_2 & a_{22} & a_{23} \\ c_3 & a_{32} & a_{33} \end{vmatrix}$$

$$y = \frac{1}{D} \begin{vmatrix} a_{11} & c_1 & a_{13} \\ a_{21} & c_2 & a_{23} \\ a_{31} & c_3 & a_{33} \end{vmatrix}$$

$$z = \frac{1}{D} \begin{vmatrix} a_{11} & a_{12} & c_1 \\ a_{21} & a_{22} & c_2 \\ a_{31} & a_{32} & c_3 \end{vmatrix}$$

Note that the numerators of these equations are obtained by replacing the column in the denominator that is associated with the unknown quantity with the coefficients on the right-hand side of the simultaneous equations. This way of writing the solution of a set of simultaneous linear equations is referred to as **Cramer's rule.**

If $c_1 = c_2 = c_3 = 0$, the equations are said to be homogeneous. If the equations are homogeneous, there is a trivial solution $x = y = z = 0$. There is a nontrivial solution only if the determinant in the denominator is equal to zero. Section 11.3, on the hydrogen molecule ion, shows that the LCAO method yields two homogeneous equations, and so multiplying out the determinant of coefficients yields a quadratic equation in the energy. The two solutions of the quadratic equation yield the energies of the bonding molecular orbital and the antibonding molecular orbital. Section 11.7 shows that there are four homogeneous equations for 1,3-butadiene, so multiplying out the determinant yields the energies of two bonding and two antibonding Hückel molecular orbitals.

D.7 VECTORS

A vector quantity has direction as well as magnitude. A vector $\boldsymbol{A}$ in a Cartesian coordinate system can be represented by

$$\boldsymbol{A} = A_x\boldsymbol{i} + A_y\boldsymbol{j} + A_z\boldsymbol{k} \tag{D.7.1}$$

where $\boldsymbol{i}, \boldsymbol{j}$, and $\boldsymbol{k}$ are vectors of unit length that point along the x, y, and z axes of the coordinate system. The coordinate systems in this book are right-handed; this means that if you move the fingers of your right hand from $\boldsymbol{i}$ to $\boldsymbol{j}$, your thumb points along $\boldsymbol{k}$. The quantities A_x, A_y, and A_z are referred to as components of A; they can be positive or negative. It follows from the Pythagorean theorem that the length of $\boldsymbol{A}$ is given by

$$A = |\boldsymbol{A}| = (A_x^2 + A_y^2 + A_z^2)^{1/2} \tag{D.7.2}$$

When vectors are added, their components in the three directions add separately. For example, if $\boldsymbol{A} = \boldsymbol{i} + \boldsymbol{j} - \boldsymbol{k}$ and $\boldsymbol{B} = \boldsymbol{i} + 2\boldsymbol{j} + 3\boldsymbol{k}$, the sum of the two vectors is $\boldsymbol{A} + \boldsymbol{B} = 2\boldsymbol{i} + 3\boldsymbol{j} + 2\boldsymbol{k}$. The addition of vectors is illustrated in Fig. 10.16.

There are two ways to form the product of two vectors: scalar product and vector product. The scalar product yields a number (a scalar), and the vector product yields a vector. The **scalar product** of $\boldsymbol{A}$ and $\boldsymbol{B}$ is defined by

$$\boldsymbol{A} \cdot \boldsymbol{B} = |\boldsymbol{A}||\boldsymbol{B}| \cos\theta \tag{D.7.3}$$

where θ is the angle between $\boldsymbol{A}$ and $\boldsymbol{B}$. This is often referred to as the dot product. The scalar product is commutative because $\boldsymbol{A} \cdot \boldsymbol{B} = \boldsymbol{B} \cdot \boldsymbol{A}$. Equation D.7.3 can be used to show that $\boldsymbol{i} \cdot \boldsymbol{i} = \boldsymbol{j} \cdot \boldsymbol{j} = \boldsymbol{k} \cdot \boldsymbol{k} = |1||1| \cos 0° = 1$ and $\boldsymbol{i} \cdot \boldsymbol{j} = \boldsymbol{j} \cdot \boldsymbol{i} = \boldsymbol{i} \cdot \boldsymbol{k} = \boldsymbol{k} \cdot \boldsymbol{i} = \boldsymbol{j} \cdot \boldsymbol{k} = \boldsymbol{k} \cdot \boldsymbol{j} = |1||1| \cos 90° = 0$. When $\boldsymbol{A}$ and $\boldsymbol{B}$ are expressed in terms of components and these equations are used, it can be shown that

$$\boldsymbol{A} \cdot \boldsymbol{B} = A_x B_x + A_y B_y + A_z B_z \tag{D.7.4}$$

There are examples of scalar products in Sections 2.1 and 15.2.

The vector product of $\boldsymbol{A}$ and $\boldsymbol{B}$ is defined by

$$\boldsymbol{A} \times \boldsymbol{B} = |\boldsymbol{A}||\boldsymbol{B}|\, \boldsymbol{c} \sin\theta \tag{D.7.5}$$

where θ is the angle between $\boldsymbol{A}$ and $\boldsymbol{B}$ and $\boldsymbol{c}$ is a unit vector perpendicular to the plane formed by $\boldsymbol{A}$ and $\boldsymbol{B}$. The direction of $\boldsymbol{c}$ is given by the right-hand rule: If the fingers of your right hand move from $\boldsymbol{A}$ to $\boldsymbol{B}$, then $\boldsymbol{c}$ is in the direction of your thumb. This is often referred to as the cross product. The cross product is not commutative because $\boldsymbol{A} \times \boldsymbol{B} = -\boldsymbol{B} \times \boldsymbol{A}$. Equation D.7.5 can be used to show that $\boldsymbol{i} \times \boldsymbol{i} = \boldsymbol{j} \times \boldsymbol{j} = \boldsymbol{k} \times \boldsymbol{k} = |1||1|\, \boldsymbol{c} \sin 0° = 0$, $\boldsymbol{i} \times \boldsymbol{j} = -\boldsymbol{j} \times \boldsymbol{i} = |1||1|\, \boldsymbol{k} \sin 90° = \boldsymbol{k}$, $\boldsymbol{j} \times \boldsymbol{k} = -\boldsymbol{k} \times \boldsymbol{j} = \boldsymbol{i}$, and $\boldsymbol{k} \times \boldsymbol{i} = -\boldsymbol{i} \times \boldsymbol{k} = \boldsymbol{k}$. When $\boldsymbol{A}$ and $\boldsymbol{B}$ are expressed in terms of components and these equations are used, it can be shown that

$$\boldsymbol{A} \times \boldsymbol{B} = (A_y B_z - A_z B_y)\boldsymbol{i} + (A_z B_x - A_x B_z)\boldsymbol{j} + (A_x B_y - A_y B_x)\boldsymbol{k} \tag{D.7.6}$$

This equation can be conveniently expressed as a determinant:

$$\boldsymbol{A} \times \boldsymbol{B} = \begin{vmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{vmatrix} \tag{D.7.7}$$

There are examples of cross products in Sections 9.12.

The following operator can be used in different ways:

$$\nabla = \boldsymbol{i}\left(\frac{\partial}{\partial x}\right)_{y,z} + \boldsymbol{j}\left(\frac{\partial}{\partial y}\right)_{x,z} + \boldsymbol{k}\left(\frac{\partial}{\partial z}\right)_{x,y} \tag{D.7.8}$$

1. If a function f is a function of x, y, and z, then ∇f (gradient of f or "grad f") is a vector:

$$\nabla f = \boldsymbol{i}\frac{\partial f}{\partial x} + \boldsymbol{j}\frac{\partial f}{\partial y} + \boldsymbol{k}\frac{\partial f}{\partial z} \tag{D.7.9}$$

2. The scalar product of ∇ with a vector $\boldsymbol{v}$ yields the divergence ("div") of that vector:

$$\nabla \cdot \boldsymbol{v} = \left(\frac{\partial v_x}{\partial x}\right) + \left(\frac{\partial v_y}{\partial y}\right) + \left(\frac{\partial v_z}{\partial z}\right) \tag{D.7.10}$$

3. The vector product of ∇ with a vector $\boldsymbol{v}$ yields the curl of the vector:

$$\nabla \times \boldsymbol{v} = \text{curl}\,\boldsymbol{v} = \boldsymbol{i}\left(\frac{\partial v_z}{\partial y} - \frac{\partial v_y}{\partial z}\right) + \boldsymbol{j}\left(\frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x}\right) + \boldsymbol{k}\left(\frac{\partial v_y}{\partial x} - \frac{\partial v_x}{\partial y}\right) \tag{D.7.11}$$

The operator ∇^2 (the Laplacian) is given in Cartesian coordinates as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{D.7.12}$$

In spherical coordinates, the Laplacian operator is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) \tag{D.7.13}$$

D.8 MATRICES*

A matrix is an array of numbers. If a matrix has m rows and n columns it may be represented by

$$\boldsymbol{A} = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & & \\ \vdots & & & \\ a_{m1} & a_{m2} & \cdots & a_{mn} \end{bmatrix}$$

The sum of two matrices is defined by

$$\boldsymbol{C} = \boldsymbol{A} + \boldsymbol{B}$$

where $c_{ij} = a_{ij} + b_{ij}$ for every i and j.

The product of a scalar c and a matrix is defined by

$$\boldsymbol{B} = c\boldsymbol{A}$$

where $b_{ij} = ca_{ij}$ for every i and j.

*G. Strang, *Linear Algebra and Its Applications,* New York: Academic, 1980; R. G. Mortimer, *Mathematics for Physical Chemistry,* New York: Macmillan, 1981.

The product of two matrices is similar to the scalar product of two vectors. If $\boldsymbol{C}$ is the product $\boldsymbol{AB}$, then

$$c_{ij} = \sum_{k=1}^{n} a_{ik} b_{kj}$$

where n is the number of columns in $\boldsymbol{A}$. If $\boldsymbol{B}$ is to be multiplied by $\boldsymbol{A}$, it must have as many rows as $\boldsymbol{A}$ has columns. For example,

$$\boldsymbol{AB} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \\ a_{31} & a_{32} \end{bmatrix} \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix} = \begin{bmatrix} a_{11}b_{11} + a_{12}b_{21} & a_{11}b_{12} + a_{12}b_{22} \\ a_{21}b_{11} + a_{22}b_{21} & a_{21}b_{12} + a_{22}b_{22} \\ a_{31}b_{11} + a_{32}b_{21} & a_{31}b_{12} + a_{32}b_{22} \end{bmatrix}$$

Matrix multiplication is not commutative, as illustrated by

$$\boldsymbol{AB} = \begin{bmatrix} 2 & 1 \\ 3 & -2 \end{bmatrix} \begin{bmatrix} 1 & 4 \\ 0 & 2 \end{bmatrix} = \begin{bmatrix} 2 \times 1 + 1 \times 0 & 2 \times 4 + 1 \times 2 \\ 3 \times 1 - 2 \times 0 & 3 \times 4 - 2 \times 2 \end{bmatrix} = \begin{bmatrix} 2 & 10 \\ 3 & 8 \end{bmatrix}$$

$$\boldsymbol{BA} = \begin{bmatrix} 1 & 4 \\ 0 & 2 \end{bmatrix} \begin{bmatrix} 2 & 1 \\ 3 & -2 \end{bmatrix} = \begin{bmatrix} 1 \times 2 + 4 \times 3 & 1 \times 1 - 4 \times 2 \\ 0 \times 2 + 2 \times 3 & 0 \times 1 - 2 \times 2 \end{bmatrix} = \begin{bmatrix} 14 & -7 \\ 6 & -4 \end{bmatrix}$$

Simultaneous linear equations may be solved by use of matrices. For example, the set

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + a_{13}x_3 &= c_1 \\ a_{21}x_1 + a_{22}x_2 + a_{23}x_3 &= c_2 \\ a_{31}x_1 + a_{32}x_2 + a_{33}x_3 &= c_3 \end{aligned}$$

may be written in matrix notation as

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix}$$

or

$$\boldsymbol{AX} = \boldsymbol{C}$$

The inverse of a matrix $\boldsymbol{A}^{-1}$ has the property

$$\boldsymbol{A}^{-1}\boldsymbol{A} = \boldsymbol{AA}^{-1} = \boldsymbol{E}$$

where $\boldsymbol{E}$ is the identity matrix:

$$\boldsymbol{E} = \begin{bmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & & & \\ 0 & 0 & & 1 \end{bmatrix}$$

If we multiply both sides of $\boldsymbol{AX} = \boldsymbol{C}$ by $\boldsymbol{A}^{-1}$, we obtain

$$\boldsymbol{A}^{-1}\boldsymbol{AX} = \boldsymbol{X} = \boldsymbol{A}^{-1}\boldsymbol{C}$$

Thus, the solution $\boldsymbol{X}$ of the simultaneous equations is obtained by multiplying $\boldsymbol{C}$ by the inverse of $\boldsymbol{A}$. Small matrices may be inverted by hand using Gauss elimination, and large matrices may be inverted with a computer to obtain the solution of the simultaneous linear equations.

If $\boldsymbol{AB} = \mathbf{0}$, $\boldsymbol{B}$ is the null space of $\boldsymbol{A}$. The null space can be calculated by hand for a small $\boldsymbol{A}$ matrix or by use of a computer. Correspondingly, $\boldsymbol{B}^T\boldsymbol{A}^T = \mathbf{0}$, where the superscript T indicates the transpose. The transpose $\boldsymbol{A}^T$ of a matrix $\boldsymbol{A}$ has columns that are taken directly from the rows of $\boldsymbol{A}$; thus it can be constructed without any calculations. Thus, $\boldsymbol{A}^T$ is the null space of $\boldsymbol{B}^T$.

D.9 COMPLEX NUMBERS

A complex number z can be written $z = x + iy$, where $i = (-1)^{1/2}$ is the imaginary unit and x and y are real numbers. x is referred to as the real part of z, and y is referred to as the imaginary part of z. It is convenient to write $x = \mathrm{Re}(z)$ and $y = \mathrm{Im}(z)$. Complex numbers arise naturally in solving certain quadratic equations.

Two complex numbers can be summed by adding the real parts and the imaginary parts separately:

$$z_1 + z_2 = (x_1 + x_2) + i(y_1 + y_2) \tag{D.9.1}$$

They can be subtracted as well:

$$z_1 - z_2 = (x_1 - x_2) + i(y_1 - y_2) \tag{D.9.2}$$

When complex numbers are multiplied, the two quantities are multiplied as binomials and i^2 is replaced by -1 to obtain

$$z_1z_2 = (x_1x_2 - y_1y_2) + i(x_2y_1 + x_1y_2) \tag{D.9.3}$$

To divide complex numbers, it is convenient to introduce the complex conjugate z^*. The **complex conjugate** z^* is obtained by changing i to $-i$. The complex conjugate of $z = x + iy$ is $z^* = x - iy$. The product of a complex number and its complex conjugate is a real number. For example,

$$zz^* = (x + iy)(x - iy) = x^2 - i^2y^2 = x^2 + y^2 \tag{D.9.4}$$

The square root of this quantity is referred to as the **absolute value** of z and is represented by $|z|$.

$$|z| = (zz^*)^{1/2} = (x^2 + y^2)^{1/2} \tag{D.9.5}$$

The ratio of two complex numbers can be written as a complex number by multiplying numerator and denominator by the complex conjugate of the denominator. For example, to find the expression for $z = (1 + 2i)/(2 + 3i)$, multiply the numerator and denominator by $(2 - 3i)$ to obtain

$$z = \frac{(8 + i)}{(4 + 9)} = \frac{8}{13} + \frac{1}{13}i \tag{D.9.6}$$

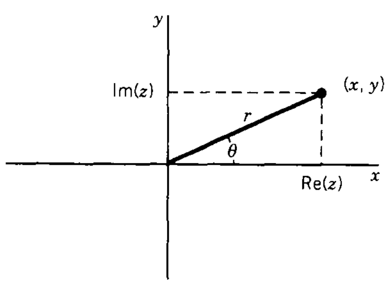

Figure D.9.1 Plot of a complex number.

A complex number can be represented as a point in a plot of $\mathrm{Im}(z)$ versus $\mathrm{Re}(z)$, as shown in Fig. D.9.1. The plane of this figure is referred to as the complex plane. The vector $\boldsymbol{r}$ from the origin to a point in the complex plane makes an angle θ with the x axis; this angle is referred to as the phase angle. The vector is represented by $\boldsymbol{r}$, and its magnitude is represented by r. It is useful to be able to write complex numbers in their polar forms. Figure D.9.1 shows that

$$x = r\cos\theta \quad \text{and} \quad y = r\sin\theta \tag{D.9.7}$$

Therefore,

$$z = r(\cos\theta + \mathrm{i}\sin\theta) \tag{D.9.8}$$

The series expansions of e^x, $\cos x$, and $\sin x$ (see Appendix D.2) can be used to derive **Euler's formula:**

$$e^{\mathrm{i}\theta} = \cos\theta + \mathrm{i}\sin\theta \tag{D.9.9}$$

If we substitute this into equation D.9.8, we obtain

$$z = re^{\mathrm{i}\theta} \tag{D.9.10}$$

for which the complex conjugate is

$$z^* = re^{-\mathrm{i}\theta} \tag{D.9.11}$$

Taking the square root of the product zz^* yields the absolute value of z, which is equal to

$$|z| = r \tag{D.9.12}$$

Two relations that are useful in connection with Fourier transforms (Section 15.8) are

$$\cos\frac{2\pi nx}{a} = (e^{\mathrm{i}2\pi nx/a} + e^{-\mathrm{i}2\pi nx/a})/2 \tag{D.9.13}$$

$$\sin\frac{2\pi nx}{a} = (e^{\mathrm{i}2\pi nx/a} - e^{-\mathrm{i}2\pi nx/a})/2\mathrm{i} \tag{D.9.14}$$

D.10 MATHEMATICAL CALCULATIONS WITH PERSONAL COMPUTERS

The use of mathematical applications in personal computers is producing a revolutionary change in solving physical chemical problems. These applications include Mathematica, MathCad, MATLAB, and MAPLE. The existence of these applications has made it possible to include more difficult problems in this edition as Computer Problems. The complete solutions of these problems in Mathematica are provided in the Solutions Manual and on the web at http://wiley.com/college/silbey. These programs not only make it possible to solve the particular problems, but they also make it possible to make similar calculations over different ranges of temperature, pressure, wavelength, etc., and to substitute the properties of other substances without one's being an expert Mathematica programmer. The primary reference on Mathematica is

S. Wolfram, *The Mathematica Book,* 4th ed. New York: Cambridge University Press, 1999.

There are two books on solving physical chemistry problems using Mathematica:

W. H. Cropper, *Mathematica Computer Programs for Physical Chemistry.* New York: Springer, 1998.
J. H. Noggle, *Physical Chemistry Using Mathematica.* New York: HarperCollins, 1996.

Several books have been written to help new users of Mathematica get started. These include

C.-K. Cheung, G. E. Keough, C. Landraitis, and R. H. Gross, *Getting Started with Mathematica.* Hoboken, NJ: Wiley, 1998.

K. R. Coombes, B. R. Hunt, R. L. Lipsman, J. E. Osborn, and G. J. Stuck, *The Mathematica Primer.* New York: Cambridge University Press, 1998.

H. F. W. Höft and M. H. Höft, *Computing with Mathematica.* San Diego: Academic, 1998.

B. F. Torrence and E. A. Torrence, *The Student's Introduction to Mathematica.* New York: Cambridge University Press, 1999.