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Applied Mathematics for Physical Chemistry

THIRD EDITION

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Preface

A perusal of many modern physical chemistry texts demonstrates that most authors of these texts and the professors who use them, such as myself, expect students to know a great deal more mathematics than is covered in the calculus courses normally required for physical chemistry courses. Moreover, we honestly expect that our students will know how to apply the mathematics they have learned to physical problems. Unfortunately, many of my colleagues and I have found that this generally is not the case. It was this observation, along with the fact that I was spending a great deal of lecture time teaching mathematics rather than physical chemistry in my physical chemistry course, that inspired me to write the first edition of this text some 30 years ago.

It is my intention, therefore, that this third edition be used as a supplement along with the student's physical chemistry textbook, to help students either review or, perhaps, learn for the first time those areas of mathematics that are essential to an understanding of physical chemistry, and, more importantly, to apply that mathematics to physical problems. The purpose of the book is *not* to replace the mathematics courses that are prerequisite to the physical chemistry course, but to be a *how to do it* review mathematics textbook. Consequently, the problems at the end of each chapter are designed to test the reader's mathematical skills, not his or her skills in solving physical chemistry problems.

Like the first two editions, the first five chapters concentrate on subject matter normally covered in prerequisite mathematics courses and should be a review. Again, an emphasis in the chapter on integral calculus has been placed on using

integral tables, and, in keeping with the original intent of the book, mathematical rigor was kept at a minimum, giving way to intuition where possible.

The latter half of the text covers important material normally not covered in prerequisite courses, but, for the most part, at an introductory level. For example, the chapter on differential equations emphasizes the solution of second-order linear differential equations with constant coefficients, common to many simple problems in wave mechanics. Also, as in the second edition, sections on the series method of solving differential equations are included. The sections on Fourier series and Fourier transforms have been expanded in this edition to include discrete Fourier transforms and well as continuous Fourier transforms. Discrete Fourier transforms are important in many areas of spectroscopy, since they can be handled by digital computers.

Finally, the chapter on numerical methods has been completely revised. In the second edition, we concentrated on writing programs using BASIC to do the numerical calculations. Over the recent years, however, there has been a move away from using compiled programs for doing scientific computations toward the use of spreadsheets, such as Microsoft Excel®, for such computations. Thus, the new chapter concentrates on using a spreadsheet to do many standard numerical calculations, such as numerical integration, fitting curves to experimental data, and finding discrete Fourier transforms of functions.

As I mentioned in the Preface to the second edition, a text such as this could not be a success without the contributions of a number of people. I especially wish to thank Professor John Bopp, Nazareth College; Professor Wayne Bosma, Bradley University; and Professor Greg Peters, University of Memphis for their careful and critical review of the second edition and their many helpful comments and suggestions. I also would like to thank Professor John Wheeler of the University of California, San Diego, for finding a serious error in one of the examples in the chapter on infinite series in the second edition that survived from the first edition.

I thank my editor John Challice, Project Manager Kristen Kaiser, Production Editor Donna Young, and all those individuals at Prentice Hall ESM and Write With, Inc. who helped to improve immensely the quality of the text.

Finally, I wish to thank my son, Stephen Barrante, who designed the cover for this edition, my wife Marlene, and our family for their patience and encouragement during the preparation of this book.

I welcome comments on the text and ask that any comments or errors found be sent to me at jrbarrante@aol.com.

JAMES R. BARRANTE

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CHAPTER

Coordinate Systems

1-1 INTRODUCTION

A very useful method for describing the functional dependency of various properties of a physicochemical system is to assign to each property a point along one of a set of axes, called a coordinate system. The choice of coordinate system used to describe the physical world will depend to a great extent on the nature of the properties being described. For example, human beings are very much "at home" in rectangular space. Look around you and note the number of 90° angles you see. Therefore, architects and furniture designers usually employ rectangular coordinates in their work. Atoms and molecules, however, live in "round" space. Generally, they operate under potentialenergy fields that are centrally located and therefore are best described in some form of "round" coordinate system (e.g., plane polar or spherical polar coordinates). In fact, many problems in physical chemistry dealing with atoms or molecules cannot be solved in linear coordinates. We shall see, however, that things we are accustomed to studying in linear coordinates, such as waves, look very different to us when they are described in polar coordinates. Once we have come to terms with polar coordinates, however, we will find that they are no more difficult to use than linear coordinates. We begin our discussion with a general treatment of linear coordinates.

1-2 CARTESIAN COORDINATES

In the mid-17th century, the French mathematician René Descartes proposed a simple method of relating pairs of numbers as points on a rectangular plane surface, today called a *rectangular Cartesian coordinate system*. A typical two-dimensional Cartesian coordinate system consists of two perpendicular axes, called the *coordinate axes*. The vertical axis generally is labeled the *y*-axis, while the horizontal axis generally is labeled the *x*-axis. The point of intersection between the two axes is called the *origin*.

¹The correct mathematical designations of the vertical axis and the horizontal axis are the *ordinate* and the *abscissa*, respectively. These terms, however, have fallen out of use over the years.

2 Chapter 1 Coordinate Systems

The application of mathematics to the physical sciences requires taking these abstract collections of numbers and the associated mathematics and relating them to the physical world. Thus, the aforementioned x's and y's could be pressures, volumes, or temperatures describing the behavior of a gas or could be any pair of physical variables related to each other. For example, Fig. 1-1 shows the relationship of the vapor pressure of water to its temperature. Note that, in designating any point on a coordinate system, the x-coordinate is always given first. Thus, the notation (333,149.4) refers to the point on the coordinate system shown in Fig. 1-1 whose T-coordinate is 333 K and whose T-coordinate is 149.4 mm Hg.

The curve depicted in Fig. 1-1 can be described by the equation $P = Ae^{-\Delta H/RT}$, where ΔH is the heat of vaporization of water, R is the gas constant, and A is a constant. The equation describing the curve could just as easily have been written $y = Ae^{-B/x}$; however, not apparent in either equation is the fact that it only approximates the behavior of the vapor pressure of a liquid with temperature, since the implied conditions that the vapor phase behave ideally and that the heat of vaporization be constant with temperature generally are not true. It is a knowledge of facts such as these that continues to distinguish the science of physical chemistry from "pure mathematics."

Coordinate systems are not limited to plane surfaces. We can extend the two-dimensional rectangular coordinate system just described into a three-dimensional coordinate system by constructing a third axis perpendicular to the *xy*-plane and passing through the origin. In fact, we are not limited to three-dimensional coordinate systems, but can extend the process to as many coordinates as we wish or need—to *n*-dimensional coordinate systems—although, as we might expect, the graphical representation becomes difficult beyond three dimensions, since we are creatures of three-dimensional space. For example, in wave mechanics, a field of physics having to do with the mechanical behavior of waves, we usually describe the

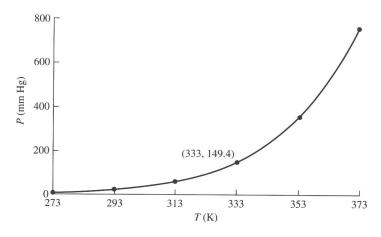


Figure 1-1 Graph of vapor pressure of water versus temperature.

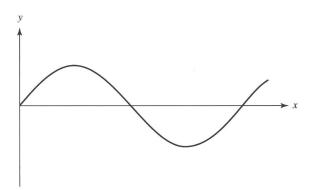


Figure 1-2 Amplitude of a one-dimensional transverse wave.

amplitude of a transverse wave by using an "extra" coordinate. Therefore, the amplitude of a one-dimensional transverse wave—say, along the *x*-axis—is represented along the *y*-axis, as illustrated for a simple sine wave in Fig. 1-2. (Keep in mind that the wave itself does not move in the *y*-direction. Rather, the wave is a disturbance, or a series of disturbances, traveling, in this case, only down the *x*-axis. We should not confuse the motion of the *wave* with the motion of the *medium producing the wave*.) A two-dimensional transverse wave in the *xy*-plane, such as a water wave moving across the surface of a lake, requires a third coordinate (call it the *z*-axis) to describe the amplitude of the wave—still easy to represent graphically and certainly within the realm of our experience. Many problems in wave mechanics, however, require us to describe the amplitudes of three-dimensional transverse waves graphically. In order to do so we need a fourth coordinate. This presents a problem to creatures of three-dimensional space, and a number of ingenious ways have been devised to get around the problem. One way is to use the density of points on a three-dimensional graph to represent the amplitude of the wave.

In any of the coordinate systems described, it is useful to define a very small, or differential, volume element

$$d\tau = dq_1 dq_2 dq_3 \dots dq_n \tag{1-1}$$

where dq_i is an infinitesimally small length along the *i*th axis. In the three-dimensional Cartesian coordinate system shown in Fig. 1-3, the volume element is simply

$$d\tau = dx \, dy \, dz \tag{1-2}$$

1-3 PLANE POLAR COORDINATES

Many problems in the physical sciences cannot be solved in rectangular space. For this reason, we find it necessary to redefine the Cartesian axes in terms of what

4 Chapter 1 Coordinate Systems

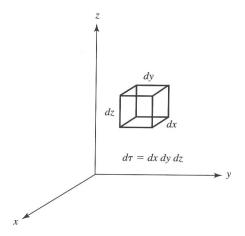


Figure 1-3 Differential volume element for a Cartesian coordinate system.

normally are referred to as "round" or "curvilinear" coordinates. Consider the diagram in Fig. 1-4. It is possible to associate every point on this two-dimensional coordinate system with the geometric properties of a right triangle. Note that the magnitude of x is the same as the length of the side b of the triangle shown and that the magnitude of y is the same as the length of the side a. Since

$$\sin \theta = \frac{a}{r}$$
 and $\cos \theta = \frac{b}{r}$ (1-3)

we can write

$$x = b = r \cos \theta$$
 and $y = a = r \sin \theta$ (1-4)

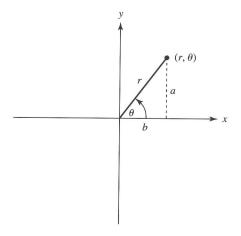


Figure 1-4 Plane polar coordinates.

Therefore, every point (x, y) of the two-dimensional coordinate system can be specified by assigning a value for r and a value for θ at that point. This type of graphical representation is called a *plane polar coordinate system*. In such a coordinate system, points are designated by the notation (r, θ) . Equations (1-4) are known as *transformation equations*; they transform the coordinates of a point from polar coordinates to Cartesian (linear) coordinates. The reverse transformation equations can be found by simple trigonometry. We have

$$\frac{y}{x} = \frac{r \sin \theta}{r \cos \theta} = \tan \theta \quad \text{or} \quad \theta = \tan^{-1} \left(\frac{y}{x}\right)$$
 (1-5)

and

$$r = (x^2 + y^2)^{1/2} (1-6)$$

1-4 SPHERICAL POLAR COORDINATES

While there are not many applications of plane polar coordinates to chemistry, one extension of plane polar coordinates to three dimensions leads to the *spherical polar coordinate system*, shown in Fig. 1-5. This system does have numerous applications to physical chemistry, particularly in those areas associated with the structure of atoms and molecules. A point in the spherical polar coordinate system is represented by three numbers: r, the distance of the point from the origin, normally called the *radius vector*; θ , the angle that the radius vector r makes with the z-axis; and ϕ , the angle that the line \overline{OA} makes with the x-axis. Since

$$\cos \phi = \frac{c}{a}, \quad \sin \phi = \frac{d}{a}, \quad \text{and} \quad \sin \theta = \frac{a}{r}$$
 (1-7)

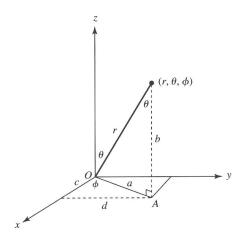


Figure 1-5 Spherical polar coordinates.

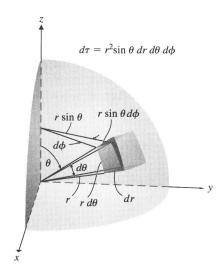


Figure 1-6 Differential volume element in spherical polar coordinates.

and since the length of c is numerically equal to x, d to y, and b to z, we can write

$$x = a \cos \phi = r \sin \theta \cos \phi$$

$$y = a \sin \phi = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$
(1-8)

The reverse transformation equations are found as follows:

$$\frac{y}{x} = \frac{r \sin \theta \sin \phi}{r \sin \theta \cos \phi} = \tan \phi \quad \text{or} \quad \phi = \tan^{-1} \left(\frac{y}{x}\right)$$
 (1-9)

$$r = (x^2 + y^2 + z^2)^{1/2} (1-10)$$

$$\cos \theta = \frac{z}{r}$$
 or $\theta = \cos^{-1} \frac{z}{(x^2 + y^2 + z^2)^{1/2}}$ (1-11)

The differential volume element in spherical polar coordinates is not as easy to determine as it is in linear coordinates. Recalling, however, that the length of a circular arc intercepted by an angle θ is $L=r\theta$, where r is the radius of the circle, we can see from Fig. 1-6 that the volume element is

$$d\tau = (dr)(r\sin\theta \, d\phi)(r\, d\theta) = r^2\sin\theta \, dr \, d\theta \, d\phi \tag{1-12}$$

Example

Determine the values of r, θ , and ϕ for the point (3, -2, 1).

Solution

$$x = 3, y = -2, \text{ and } z = 1:$$

$$r = \sqrt{x^2 + y^2 + z^2} = \sqrt{9 + 4 + 1} = \sqrt{14} = 3.742$$

$$\theta = \cos^{-1}\left(\frac{z}{r}\right) = \cos^{-1}\left(\frac{1}{3.742}\right) = 74.50^{\circ}$$

$$\phi = \tan^{-1}\left(\frac{y}{x}\right) = \tan^{-1}\left(\frac{-2}{3}\right) = -33.69^{\circ}$$

1-5 COMPLEX NUMBERS

A *complex number* is a number composed of a real part x and an imaginary part iy, where $i = \sqrt{-1}$. A complex number is thus represented by the equation z = x + iy. Actually, *all* numbers are complex numbers and can be described by the same equation; it is just that for real numbers, y = 0, while for pure imaginary numbers, x = 0.

Like real numbers, complex numbers can be represented on a coordinate system. The real part of the complex number is designated along the *x*-axis, while the pure imaginary part is designated along the *y*-axis, as shown in Fig. 1-7. Since $x = r \cos \theta$ and $y = r \sin \theta$, any complex number can be written as

$$z = x + iy = r\cos\theta + ri\sin\theta = r(\cos\theta + i\sin\theta)$$
 (1-13)

Moreover, since every point in the plane formed by the *x*- and *y*-axes represents a complex number, the plane is called the *complex plane*. In an *n*-dimensional coordinate system, one plane may be the complex plane.

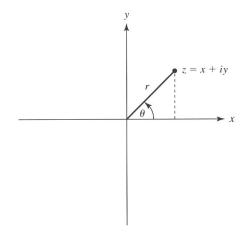


Figure 1-7 The complex plane.

The value of r in Equation (1-13), called the *modulus* or *absolute value*, can be found by the equation

$$r = (x^2 + y^2)^{1/2} = |z|$$
 (1-14)

The angle θ , called the *phase angle*, simply describes the rotation of z in the complex plane. The square of the absolute value can be shown to be identical to the product of z = x + iy and its complex conjugate $z^* = x - iy$. The complex conjugate of a complex number is formed by changing the sign in front of the imaginary part. The product of a complex number and its complex conjugate is *always* a real number:

$$z^* z = (x - iy)(x + iy) = x^2 + y^2 = |z|^2$$
 (1-15)

To find another useful relationship between $\sin \theta$ and $\cos \theta$ in the complex plane, let us expand each function in terms of a Maclaurin series. (Series expansions are covered in detail in Chapter 6.) We have

$$\sin \theta = \theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} - \frac{\theta^7}{7!} + - \dots$$
 (1-16)

$$\cos \theta = 1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} - \frac{\theta^6}{6!} + - \dots$$
 (1-17)

where n! (n factorial) is n! = (1)(2)(3)(4)...(n-1)(n). Hence,

$$\cos\theta + i\sin\theta = 1 + i\theta - \frac{\theta^2}{2!} - \frac{i\theta^3}{3!} \cdots$$
 (1-18)

But this is identical to the series expansion for $e^{i\theta}$:

$$e^{i\theta} = 1 + i\theta - \frac{\theta^2}{2!} - \frac{i\theta^3}{3!} \dots$$
 (1-19)

Hence, we can write

$$e^{i\theta} = \cos\theta + i\sin\theta \tag{1-20}$$

and

$$z = re^{i\theta} \tag{1-21}$$

By the same method, it can be shown that

$$e^{-i\theta} = \cos\theta - i\sin\theta \tag{1-22}$$

and

$$z^* = re^{-i\theta} \tag{1-23}$$

Equations (1-20) and (1-22) are known as Euler's (pronounced "oiler's") relations.

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