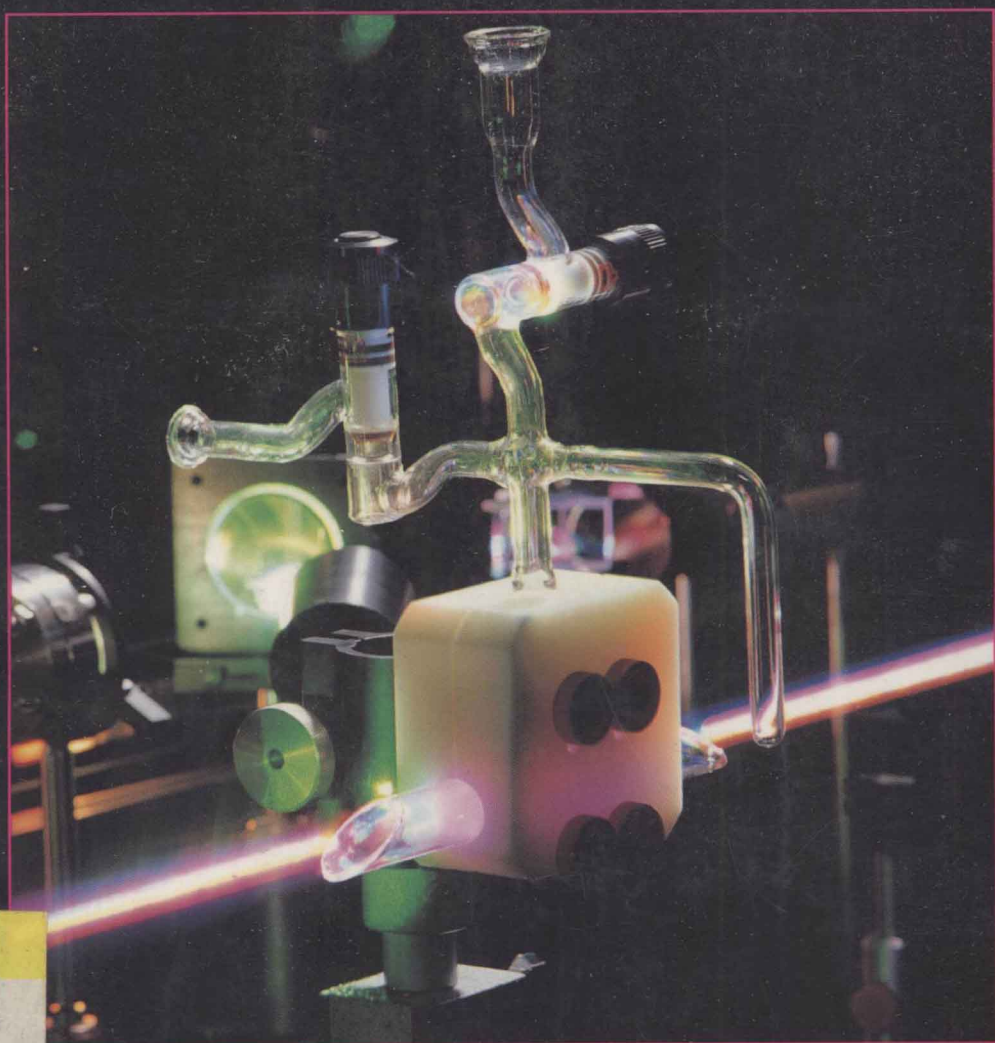


# THE PHYSICAL BASIS OF CHEMISTRY



WARREN S. WARREN

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\_\_\_\_\_ CHEMISTRY

## **Preface**

*Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry. If mathematical analysis should ever hold a prominent place in chemistry— an aberration which is happily almost impossible— it would occasion a rapid and widespread degeneration of that science.*

*Auguste Comte (1798-1857)  
in Philosophie Positive (1830)*

*I am convinced that the future progress of chemistry as an exact science depends very much upon the alliance with mathematics.*

*A. Frankland (1825-1899)  
in Amer. J. Math. 1, 349(1878)*

Frankland was correct.

This book is mainly intended as a supplement for the mathematically sophisticated topics in an advanced freshman chemistry course. My intent is not to force-feed math and physics into the chemistry curriculum; it is to reintroduce just enough to make important results *understandable* (or, in the case of quantum mechanics, surprising). We have tried to produce a high-quality yet affordable volume, which can be used in conjunction with any general chemistry book. This lets the instructor choose whichever general chemistry book covers basic concepts and descriptive chemistry in a way which seems most appropriate for the students. The book might also be used for the introductory portions of a junior-level course for students who have not taken multivariate calculus, or who do not need the level of rigor associated with the common one-year junior level physical chemistry sequence; for example, an introduction to biophysical chemistry or materials science should build on a foundation which is essentially at this level.

The book grew out of supplementary lecture notes from the five years I taught advanced general chemistry at Princeton University. Placement into this course is based almost exclusively on math SAT scores—no prior knowledge of chemistry is assumed. Most of the students become science or engineering majors, and they have a broad range of interests, but the strongest common denominator is interest in and aptitude for mathematics.

Picking a text book for this group of students proved to be a difficult problem. The most important change in freshman chemistry books over the

last decade has been the introduction of color to illustrate descriptive chemistry. The importance of this advance should not be minimized—it helps bring out the elegance that exists in the practical aspects of chemistry. However, it has dramatically increased the cost of producing textbooks, and as a result it has become important to "pitch" these books to the widest possible audience. In general that has meant a reduction in the level of mathematics. Most modern textbooks mainly differ in the order of presentation of the material and the style of the chapters on descriptive chemistry—and almost all of them omit topics which require a little more mathematical sophistication. Thus the challenge to us was to keep the strong coverage of descriptive chemistry characteristic of the best modern texts, yet elevate the mathematical level to something more appropriate for our better students.

In fact, many important aspects of chemistry can only be memorized, not understood, without appeal to mathematics. For example:

—The basic principles behind classical mechanics are quite familiar to most of these students. Almost all of them have used  $F=ma$ , or can understand that a charge going around in a circle is a current. It is easy to use only these concepts to prove that something is wrong with any classical interpretation of atomic and molecular structure. Quantum mechanics allows us to predict the structure of atoms and molecules in a manner which agrees extremely well with experimental evidence, but the intrinsic logic cannot be understood without equations.

—The structure of molecules is generally explained by concepts which are simple and usually correct (for example, VSEPR theory), but clearly based on some very stringent assumptions. However, the test of these theories is their agreement with experiment. It is important to understand that modern spectroscopic techniques let us measure the structures of molecules to very high precision, but only because the experimental data can be given a theoretical foundation.

—Statistics play a central role in chemistry, because we essentially never see *one* molecule decompose, or *two* molecules collide. When 1g of hydrogen gas burns in oxygen to give water,  $6 \times 10^{23}$  hydrogen atoms undergo a fundamental change in their energy and electronic structure! The properties of the reactive mixture can only be understood in terms of averages. There is no such thing as the pressure, entropy or temperature of a single helium

atom–yet temperature, entropy and pressure are macroscopic, measurable, averaged quantities of great importance.

The concepts of equilibrium as the most probable state of a very large system, the size of fluctuations about that most probable state, and entropy (randomness) as a driving force in chemical reactions, are very useful and not that difficult. We develop the Boltzmann distribution and use this concept in a variety of applications.

In all cases, I assume that the students have a standard general chemistry book at their disposal. Color pictures of exploding chemical reactions (or for that matter, of hydrogen atom line spectra and lasers) are nice, but they are already contained in all of the standard books. Thus color is not used here. The background needed for this book is a "lowest common denominator" for the standard general chemistry books; in addition, I assume that students using this book are at least taking the first semester of calculus concurrently.

Chapters 1-3 develop the mathematical, physical and statistical tools needed for this book. I use derivatives of one variable extensively. I also use the *concept* of integration as a way to determine the area under a curve, but the students are only asked to gain a qualitative understanding. Multivariate calculus is not used.

Chapter 4 covers the kinetic theory of gases, and would probably fit best after students have covered the standard material on gases in a general chemistry book (applications of  $PV=nRT$ , definition of pressure, and so forth). Material in this chapter is not required later in the book, so it can be covered later if desired.

Chapter 5 takes the student through fundamental quantum mechanics. The perspective is quite different than what is found in most texts; I *want* students to be surprised by the results of quantum mechanics, and to think at least a little about the philosophical consequences.

Chapter 6 introduces Schrödinger's equation and rationalizes more advanced concepts, such as hybridization, molecular orbitals, and multielectron atoms. It is written at a somewhat more sophisticated level than is the rest of the book. It is most appropriate for the more advanced students who might use this text.

Chapter 7 provides a very broad overview of molecular spectroscopy and the origins of color. The topics range all the way from rainbows and peacock feathers to microwave ovens and the greenhouse effect. Once again, the emphasis is on obtaining an understanding of how we know what we know about molecules, with mathematics kept a minimum in most sections.

I wish to thank the students who have used previous versions of this book, and have often been diligent in finding errors; and Randy Bloodsworth, who found still more of the errors I missed. Useful suggestions have come from a variety of experienced instructors over the last few years, most notably Professor Walter Kauzmann and the late Miles Pickering, Director of Undergraduate Laboratories at Princeton.

Any suggestions or corrections would be appreciated. I hope that the students learn even half as much by using this book as I did by writing it.

*Warren S. Warren*  
Princeton, New Jersey  
May 1993



*To Kathy, Julie, and Michael, for their patience*

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## **Chapter I. The Tools of the Trade: Mathematical Concepts**

*No human investigation can be called real science if it cannot be demonstrated mathematically*

*Leonardo da Vinci (1452-1519)*

This chapter is intended to review a variety of basic results from high school algebra and trigonometry which are useful for understanding physical and chemical concepts. It also introduces some of the most fundamental results of a first-year college calculus course. It is obviously impossible to cover all of these topics in depth in the space available here; however, references are given at the end of most sections to "Additional Readings", listed at the end of the book, which provide far more detail.

### **1.1 Units of Measurement**

Chemistry and physics are experimental sciences, based on measurements. Our characterization of molecules, and everything else in the universe around us, rests on observable physical quantities whose values are expressed in units which ideally would be precise, convenient and reproducible. These three requirements have always produced tradeoffs. For example, the English unit of length "inch" was defined to be the length of three barleycorns laid end to end—a convenient and somewhat reproducible standard for an agricultural society. When the metric system was developed in the 1790s, the meter was defined to be 1/10,000,000 of the best current estimate of distance from the equator to the North Pole along the Prime Meridian. This definition lacked convenience; the *practical* definition was based on the distance between two scratches on a platinum-iridium bar. This bar was termed the "primary standard;" copies (secondary standards) were calibrated against the original and then taken to other laboratories.

The most important modern system of units is the SI system, which is based around seven primary units: time (second, abbreviated s); length (meter, m), mass (kilogram, kg), temperature (Kelvin, K), current (Amperes, A), amount of substances (mole, mol) and luminous intensity (candela, cd). The candela is mainly important for characterizing radiation sources, such as light bulbs. Most of the primary units are no longer defined by physical artefacts such as the platinum-iridium bar mentioned above. For example, the second is defined in terms of a specific frequency of radiation which causes atoms of the isotope cesium-133 to absorb energy. This radiation is defined to oscillate at a frequency of 9,192,631,770 Hertz— in other words, an instrument which counts 9,192,631,770 cycles of this wave will have measured exactly one

second. Commercially available "cesium clocks" use this principle, and are accurate to a few parts in  $10^{14}$ .

In addition, the meter is defined to be the distance light travels in a vacuum during  $1/299,793,238$  of a second. Thus the speed of light  $c$  is *exactly* 299,793,238 meters per second; we abbreviate this as  $\text{m}\cdot\text{s}^{-1}$ , where the "." separates the different units, which are all expressed with positive or negative exponents. More accurate measurements in the future will sharpen the definition of the meter, not change this numerical value. This inconvenient numerical value was chosen instead of (for example) exactly  $3 \times 10^8 \text{ m}\cdot\text{s}^{-1}$  because both the meter and the second predated the modern definitions, so the value was calculated to allow improved accuracy while remaining as consistent as possible with previous measurements.

All other physical quantities have units which are combinations of the primary units. Some of these *secondary units* have names of their own. The most important of these for our purposes are listed in Table 1.1 below.

**Table 1.1 Common SI secondary quantities and their units**

<u>Secondary quantity</u>	<u>Abbreviation</u>	<u>Unit</u>	<u>Equivalent in other units</u>
Charge	q	Coulomb (C)	$\text{A}\cdot\text{s}$
Energy	E; U; K	Joule (J)	$\text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}$
Frequency	$\nu$	Hertz (Hz)	$\text{s}^{-1}$
Force	F	Newton (N)	$\text{kg}\cdot\text{m}\cdot\text{s}^{-2}$
Pressure	P	Pascal (Pa)	$\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-2}$ , or force per unit area
Power or intensity	I	Watt (W)	$\text{kg}\cdot\text{m}^2\cdot\text{s}^{-3}$ , or energy per second

Other systems of units for primary and secondary quantities are also sometimes useful. For example, the ideal gas law  $PV=nRT$  is often written with pressures in units such as atmospheres (atm;  $1 \text{ atm} = 101,325 \text{ Pa}$ ), or units of torr, based on the pressure exerted by a 1 mm column of mercury ( $1 \text{ atm}$  is the same as the pressure exerted by 760 mm of mercury, so we write  $1 \text{ atm} = 760 \text{ torr}$ ).

Note that the kilogram, not the gram, is the primary unit of mass in the SI system. Prefixes can be used with all of the primary and secondary units to change their values by powers of ten. Other prefixes we will encounter are listed in Table 1.2 below.

**Table 1.2 Common prefixes**

<u>Prefix</u>	<u>Example</u>	<u>Numerical Factor</u>
femto-	femtosecond (fs)	$10^{-15}$
pico-	picomole (pmol)	$10^{-12}$
nano-	nanometer (nm)	$10^{-9}$
micro-	micromolar ( $\mu\text{M}$ )	$10^{-6}$
milli-	milliliter (mL)	$10^{-3}$
—		$10^0$
kilo-	kilogram (kg)	$10^3$
mega-	megapascal (MPa)	$10^6$
giga-	gigawatt (GW)	$10^9$
tera-	terahertz (THz)	$10^{12}$

Note the abbreviations for the units. **Capitalization is important.** Meters and moles per liter (molar), or mill- and mega-, differ only by capitalization. For  $10^{-6}$  the prefix includes the Greek letter  $\mu$ . The common convention is to use these prefixes in preference to the intermediate values. Thus, 10 mm or .01 m is preferred to 1 cm. However, for historical reasons some of the intermediate units are still commonly used- for example, atomic dimensions are frequently specified in Angstroms ( $\text{\AA}$ ;  $1\text{\AA}=10^{-10}\text{ m}=100\text{ pm}$ ).

For further information on SI units, prefixes, and conversion constants: see section 1 of reference [1].

## 1.2 Trigonometric Functions

When we have an equation such as  $y=x^2 -3x +2$ , we say that  $y$  is a function of  $x$ , written  $y=f(x)$ , which means that for any value of  $x$  there is a unique value of  $y$ . The converse need not be true; for example,  $y=x^2$  has only one value of  $y$  associated with a single value of  $x$ , but two values of  $x$  (plus and minus) associated with a single positive value of  $y$  and no values of  $x$  associated with a negative value of  $y$  (ignoring imaginary numbers, as we will try to do throughout this book).

Some of the most important functions we will encounter are the *trigonometric functions*. Consider the equation  $x^2 + y^2 =1$ . The set of all points in a plane which satisfy this equation is a circle with radius 1 (Figure 1.1). Any position on the circle could be labeled by the length  $\theta$  of the arc which stretches counterclockwise from the positive  $x$ -axis to that point. Since the circle has circumference  $2\pi$ , only values of  $\theta$  between 0 and  $2\pi$  are needed

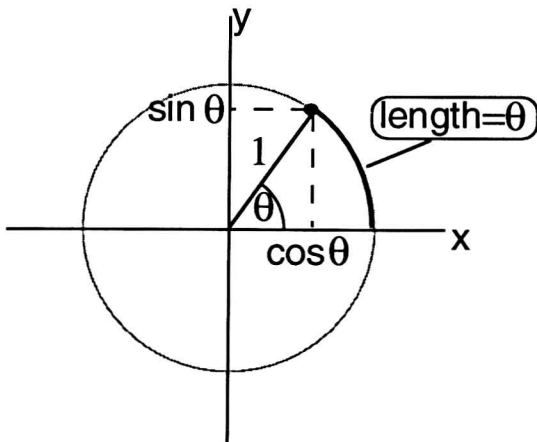


Figure 1.1 Definition of the sine and cosine function, in terms of positions on a circle with radius 1.

to describe the whole circle. We can give the same label  $\theta$  to the angle which creates this arc; in this case, we refer to the angle in units of *radians*, and  $2\pi$  radians corresponds to a complete circle.

Radians might seem superficially to be an inconvenient unit for measuring angles. In fact, however, they turn out to be the most natural unit, as we will see when we discuss derivatives later in this chapter. The  $x$ -coordinate of the ball is *defined* to be the cosine of the angle  $\theta$ , written  $\cos \theta$ ; the  $y$ -coordinate is *defined* to be the sine of the angle  $\theta$ , written  $\sin \theta$ . Inspection of Figure 1.1 shows that  $\sin^2 \theta + \cos^2 \theta =1$ .

Now suppose we move counter-clockwise along the circle at a constant speed, which we will call  $\omega$ ;  $\omega$  has units of radians per second, and is also called the *angular velocity*. The  $x$  and  $y$  coordinates will vary with time as



shown in Figure 1.2. Notice that the waveform is the same for the cosine (x coordinate) and the sine (y coordinate) except for a shift of one-quarter cycle. One complete cycle requires a time  $T=2\pi/\omega$ , which we call the *period* of the sine wave. The *frequency* of the sine wave, conventionally called  $\nu$ , is one cycle in  $2\pi/\omega$  seconds. Thus we can write:

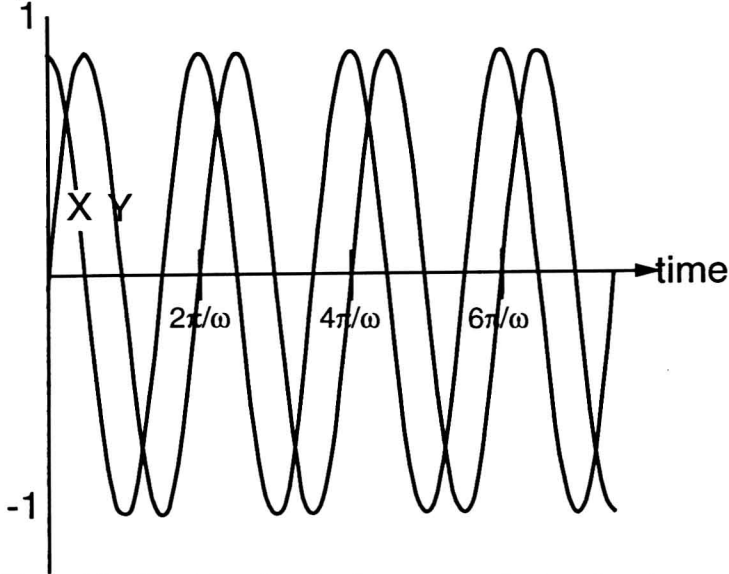


Figure 1.2. Sine (y) and cosine (x) components of motion at a constant angular velocity  $\omega$  along a circular path.

$$\nu = (1 \text{ cycle}) / (2\pi/\omega \text{ seconds}) = \omega/2\pi \text{ cycles per second.} \quad [1.1]$$

In addition to the sine and cosine, four other trigonometric functions are commonly used:

$$\text{Tangent: } \tan \theta \equiv \sin \theta / \cos \theta;$$

$$\text{Cotangent: } \cot \theta \equiv \cos \theta / \sin \theta;$$

$$\text{Secant: } \sec \theta \equiv 1 / \cos \theta;$$

$$\text{Cosecant: } \csc \theta \equiv 1 / \sin \theta \quad [1.2]$$

Note the use of the character " $\equiv$ " in these equations, which means "is defined to be equal to".