SUGGESTED READING

See also the suggested reading list for Chapter 9.

The following books and articles deal with special aspects of composite mechanisms.

P. G. Ashmore, *Catalysis and Inhibition of Chemical Reactions,* London: Butterworth, 1963.

R. P. Bell, *Acid-Base Catalysis,* Oxford: Clarendon Press, 1941.

W. P. Jencks, *Catalysis in Chemistry and Enzymology,* New York: McGraw-Hill, 1969; Dover edition, 1987.

K. J. Laidler, "Rate-controlling step: a necessary or useful concept?", *J. Chem. Education,* **65,** 250–254 (1988). In this article some of the pitfalls in deciding on a rate-controlling step are pointed out. It is argued that it is not necessary to worry about identifying a rate-controlling step, and that it is better not to do so if there are any uncertainties about the identification.

K. J. Laidler and P. S. Bunting, *The Chemical Kinetics of Enzyme Action* (2nd ed.), Oxford: Clarendon Press, 1973.

G. J. Minkoff and C. F. H. Tipper, *Chemistry of Combustion Reactions,* London: Butterworth, 1962.

J. R. Murdoch, "What is the rate-limiting step of a multistep reaction?" *J. Chemical Education,* **58**, 32–36 (1981). This article gives a particularly clear analysis of the problem of deciding upon a rate-controlling step when there are a number of consecutive steps.

R. P. Wayne, *Principles and Applications of Photochemistry,* Oxford: University Press, 1988.

The many volumes of *Comprehensive Chemical Kinetics,* Amsterdam: Elsevier, which have appeared regularly since 1969, cover most aspects of kinetics in considerable detail.

So far we have developed physical chemistry with little regard to the existence of the fundamental particles that comprise all matter. This approach reveals a good deal about the properties of matter, but much more can be accomplished on the basis of the laws that govern the behavior of these fundamental particles. During the 1930s it became apparent that more progress is made by considering the *wave properties* of particles, and we will therefore begin by summarizing what is known about wave motion.

11.1 ELECTROMAGNETIC RADIATION AND THE OLD QUANTUM THEORY

Visible light and many other apparently different types of radiation are all forms of *electromagnetic radiation,* and in a vacuum they all travel with the same speed, namely 2.998×10^8 metres per second ($m\ s^{-1}$). Electromagnetic radiation is characterized by a **wavelength** λ and a **frequency** ν. These two physical quantities are related to the speed of light c by the equation

Wavelength and Frequency

$$\lambda\nu = c \tag{11.1}$$

The SI unit of wavelength is the metre, although multiples such as nanometres (nm) are frequently used, especially in spectroscopy (Chapter 13). The SI unit of frequency is the reciprocal second (s^{-1}), which is also called the *hertz* (Hz).

Because of this relationship, all electromagnetic radiation can be classified in terms of either its wavelength or its frequency, as is done in Figure 11.1. We see that long radio waves and electric waves may have wavelengths of many kilometres and very low frequencies, whereas γ (gamma) rays have very high frequencies and extremely short wavelengths.

Electromagnetic radiation differs from certain other types of waves in a number of important respects. Sound waves, water waves, seismic waves, and waves in a plucked guitar string exist only by virtue of the medium in which they occur, whereas electromagnetic waves can travel in a vacuum. Sound waves traveling through a gas, for example, consist of alternating zones of compression and rarefaction, and the molecular displacements that occur are in the direction in which the wave travels. As the wave passes a certain region, the gas molecules undergo changes in energy and momentum which then pass on to the next region. This type of wave propagation is also found with a seismic wave traveling through the earth.

An electromagnetic wave is essentially different, since it can travel through a vacuum, and the medium is not essential. However, when such a wave comes in contact with matter, there are important interactions that affect the wave and the material. There is a coupling of the radiation with the medium, and how this occurs is best considered with reference to Figure 11.2, which shows that the wave has two components, one an electric field and the other a magnetic field. These components are in two planes at right angles to each other. A given point in space experiences a periodic disturbance in electric and magnetic field as the wave passes by. A charged particle such as an electron couples its charge with these field fluctuations and oscillates with the frequency of the wave. A useful analogy is provided by a cork and therefore

$$\omega = (2\pi \text{ rad})\nu \tag{11.4}$$

The mathematical form of the displacement y, shown in Figure 11.3b, is

$$y = A \sin(\omega t) \tag{11.5}$$

Phase

where the quantity ωt (unit: radian) is called the **phase.** More generally, we can allow a displacement by the angle δ before simple harmonic motion begins, as shown in Figure 11.3c. This displacement δ is known as the **phase constant** and this modification requires that

$$y = A \sin(\omega t + \delta) \tag{11.6}$$

The corresponding variation of y with t is shown in Figure 11.3d. Since the curves are not superimposable without a *phase shift,* they are said to be *out of phase.*

To obtain the *acceleration* of point P we differentiate this equation twice:

$$\frac{d^2y}{dt^2} = -A\omega^2 \sin(\omega t + \delta) \tag{11.7}$$

Elimination of $A \sin(\omega t + \delta)$ between these last two equations gives the equation

$$\frac{d^2y}{dt^2} = -\omega^2 y \tag{11.8}$$

Simple Harmonic Motion

This is the equation for **simple harmonic motion.**

Any motion obeying Eq. 11.8 is referred to as simple harmonic motion. Such motion is also found with a mass attached to the end of a spring in which the restoring force obeys *Hooke's law,* which means that it is proportional to the displacement y:

Hooke's Law

$$F = -k_h y \tag{11.9}$$

where k_h is the *force constant.* According to Newton's second law of motion this force is the mass m times the acceleration d^2y/dt^2:

$$F = m\frac{d^2y}{dt^2} \tag{11.10}$$

Equating these two expressions for F gives

$$\frac{d^2y}{dt^2} = \frac{-k_h}{m}y \tag{11.11}$$

To solve this we need a function y that when differentiated twice gives the function back again. This condition is satisfied by the sine and cosine functions or by combinations of them. For simplicity we choose the sine function,

$$y = a \sin\left(\sqrt{\frac{k_h}{m}}t + b\right) \tag{11.12}$$

Double differentiation gives

$$\frac{d^2y}{dt^2} = -\frac{k_h}{m}a \sin\left(\sqrt{\frac{k_h}{m}}t + b\right) = -\frac{k_h}{m}y \tag{11.13}$$

Our chosen function has therefore satisfied Eq. 11.11. The choices of a and b in Eq. 11.12 are arbitrary and can be determined from initial conditions. Equation 11.12 becomes identical with Eq. 11.6 if a is the amplitude A, if b is the initial phase angle δ, and if

$$\sqrt{\frac{k_h}{m}} = \omega/\text{rad} \tag{11.14}$$

Substitution into this expression of the value of ω from Eq. 11.4 gives

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k_h}{m}} \tag{11.15}$$

This frequency, known as the **natural frequency** of the simple harmonic motion, thus varies inversely with the square root of the mass.

EXAMPLE 11.1 Suppose that a hydrogen atom (mass = 1.67×10^{-27} kg) is attached to the surface of a solid by a bond having a force constant of 5.0 kg s^{-2}. Calculate the frequency of its vibration.

Solution From Eq. 11.15 it follows that

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k_h}{m}} = \frac{1}{2\pi}\sqrt{\frac{5.0\ (\text{kg s}^{-2})}{1.67 \times 10^{-27}\ (\text{kg})}}$$
$$= 8.70 \times 10^{12}\ \text{s}^{-1}$$

When a body is oscillating, its kinetic energy E_k and its potential energy E_p are continuously varying, but their sum E_{total} is a constant:

$$E_{\text{total}} = E_k + E_p \tag{11.16}$$

We have seen (Eq. 1.12) that the potential energy is the work done in moving a mass from its equilibrium position to a new position; thus for the displacement y from the equilibrium position

$$E_p = \int_0^y (-F)\,dy = \int_0^y k_h y\,dy = \frac{k_h y^2}{2} \tag{11.17}$$

The kinetic energy is $\frac{1}{2}mu^2$ where u is the velocity. We can evaluate the total energy by calculating its value when the oscillator reverses its direction; then $u = 0$ and $y = A$, the maximum amplitude. The potential energy is then $\frac{1}{2}k_h A^2$ (Eq. 11.17) and