THE CHEMIST'S TOOLKIT 18 The classical harmonic oscillator

A **harmonic oscillator** consists of a particle of mass m that experiences a 'Hooke's law' restoring force, one that is proportional to the displacement of the particle from equilibrium. An example is a particle of mass m attached to a spring or an atom attached to another by a chemical bond. For a one-dimensional system,

$$F_x = -k_f x \qquad (18.1)$$

where the constant of proportionality is called the **force constant**. From Newton's second law of motion ($F = ma = m(d^2x/dt^2)$; see *The chemist's toolkit* 3),

$$m\frac{d^2x}{dt^2} = -k_f x \qquad (18.2)$$

If $x = 0$ at $t = 0$, a solution (as may be verified by substitution) is

$$x(t) = A \sin 2\pi\nu t \qquad \nu = \frac{1}{2\pi}\left(\frac{k_f}{m}\right)^{1/2} \qquad (18.3)$$

This solution shows that the position of the particle oscillates *harmonically* (i.e. as a sine function) with frequency ν (units: Hz) and that the frequency of oscillation is high for light particles (m small) attached to stiff springs (k_f large). It is useful to define the *angular frequency* as $\omega = 2\pi\nu$ (units: radians per second). It follows that the angular frequency of a classical harmonic oscillator is $\omega = (k_f/m)^{1/2}$.

The negative sign in the expression for the force implies that it is negative (directed toward negative x) if the displacement is positive, and vice versa. Potential energy V is related to force by $F = -dV/dx$ (*The chemist's toolkit* 6), so the potential energy corresponding to a Hooke's law restoring force is

$$V(x) = \tfrac{1}{2}k_f x^2 \qquad (18.4)$$

Such a potential energy is called a 'harmonic potential energy' or a 'parabolic potential energy'.

As the particle moves away from the equilibrium position its potential energy increases and so its kinetic energy, and hence its speed, decreases. At some point all the energy is potential and the particle comes to rest at a turning point. The particle then accelerates back towards and through the equilibrium position. The greatest probability of finding the particle is where it is moving most slowly, which is close to the turning points.

The turning point, x_{tp}, of a classical oscillator occurs when its potential energy $\tfrac{1}{2}k_f x^2$ is equal to its total energy, so

$$x_{tp} = \pm\left(\frac{2E}{k_f}\right)^{1/2}$$

The turning point increases with the total energy: in classical terms, the amplitude of the swing of a pendulum or the displacement of a mass on a spring increases.