THE CHEMIST'S TOOLKIT 7 The equipartition theorem

The Boltzmann distribution (see the *Prologue* in the text) can be used to calculate the average energy associated with each mode of motion of an atom or molecule in a sample at a given temperature. However, when the temperature is so high that many energy levels are occupied, there is a much simpler way to find the average energy, through the **equipartition theorem**:

> For a sample at thermal equilibrium the average value of each quadratic contribution to the energy is $\frac{1}{2}kT$.

A 'quadratic contribution' is a term that is proportional to the square of the momentum (as in the expression for the kinetic energy, $E_k = p^2/2m$; *The chemist's toolkit* 6) or the displacement from an equilibrium position (as for the potential energy of a harmonic oscillator, $E_p = \frac{1}{2}k_f x^2$). The theorem is a conclusion from classical mechanics and for quantized systems is applicable only when the separation between the energy levels is so small compared to kT that many states are populated. Under normal conditions the equipartition theorem gives good estimates for the average energies associated with translation and rotation. However, the separation between vibrational and electronic states is typically much greater than for rotation or translation, and for these types of motion the equipartition theorem is unlikely to apply.