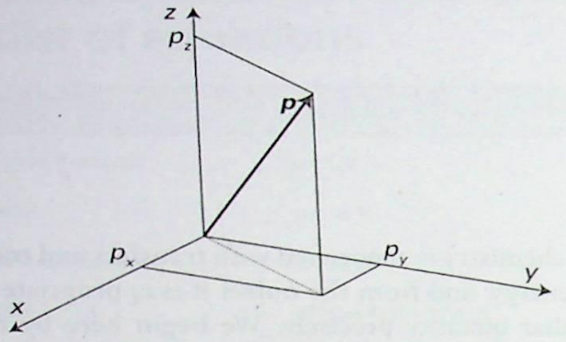

Figure B.1 The linear momentum p is denoted by a vector of magnitude p and an orientation that corresponds to the direction of motion.

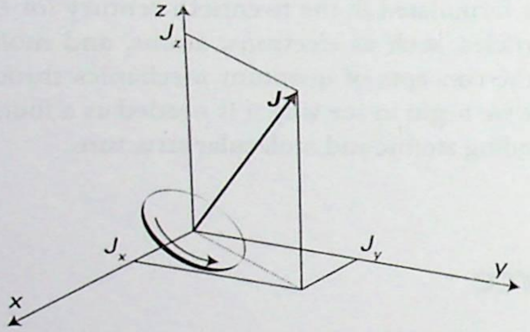

Figure B.2 The angular momentum J of a particle is represented by a vector along the axis of rotation and perpendicular to the plane of rotation. The length of the vector denotes the magnitude J of the angular momentum. The direction of motion is clockwise to an observer looking in the direction of the vector.

momentum is a vector: its magnitude gives the rate at which a particle circulates and its direction indicates the axis of rotation (Fig. B.2). The magnitude of the angular momentum, J, is

$$J = I\omega$$

Angular momentum (B.3)

where ω is the **angular velocity** of the body, its rate of change of angular position (in radians per second), and I is the **moment of inertia**, a measure of its resistance to rotational acceleration. For a point particle of mass m moving in a circle of radius r, the moment of inertia about the axis of rotation is

$$I = mr^2$$

Point particle Moment of inertia (B.4)

Brief illustration B.1 The moment of inertia

There are two possible axes of rotation in a $C^{16}O_2$ molecule, each passing through the C atom and perpendicular to the axis of the molecule and to each other. Each O atom is at a distance R from the axis of rotation, where R is the length of a CO bond, 116 pm. The mass of each ^{16}O atom is $16.00m_u$, where $m_u = 1.660\,54 \times 10^{-27}$ is the atomic mass constant. The C atom is stationary (it lies on the axis of rotation) and does not contribute to the moment of inertia. Therefore, the moment of inertia of the molecule around the rotation axis is

$$I = 2m(^{16}O)R^2 = 2\times\left(\overbrace{16.00\times\overbrace{1.660\,54\times10^{-27}\,\text{kg}}^{m_u}}^{m(^{16}O)}\right)\times\left(\overbrace{1.16\times10^{-10}\,\text{m}}^{R}\right)^2$$

$$= 7.15\times10^{-46}\,\text{kg}\,\text{m}^2$$

Note that the units of moments of inertia are kilograms-metre squared (kg m²).

Self-test B.1 The moment of inertia for rotation of a hydrogen molecule, $^1H_2$, about an axis perpendicular to its bond is $4.61\times10^{-48}\,\text{kg}\,\text{m}^2$. What is the bond length of H_2?

Answer: 74.14 pm

(b) Newton's second law of motion

According to **Newton's second law of motion**, *the rate of change of momentum is equal to the force acting on the particle*:

$$\frac{dp}{dt} = F$$

Newton's second law of motion (B.5a)

For motion confined to one dimension, we would write $dp_x/dt = F_x$. Equation B.5a may be taken as the definition of force. The SI units of force are newtons (N), with

$$1\,\text{N} = 1\,\text{kg}\,\text{m}\,\text{s}^{-2}$$

Because $p = m(dr/dt)$, it is sometimes more convenient to write eqn B.5a as

$$ma = F \qquad a = \frac{d^2r}{dt^2}$$

Alternative form Newton's second law of motion (B.5b)

where a is the **acceleration** of the particle, its rate of change of velocity. It follows that if we know the force acting everywhere and at all times, then solving eqn B.5 will give the **trajectory**, the position and momentum of the particle at each instant.

Brief illustration B.2 Newton's second law of motion

A *harmonic oscillator* consists of a particle that experiences a 'Hooke's law' restoring force, one that is proportional to its displacement 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, $F_x=-k_f x$, where the constant of proportionality k_f is called the *force constant*. Equation B.5b becomes

$$m\frac{d^2x}{dt^2}=-k_f x$$

(Techniques of differentiation are reviewed in *Mathematical background* 1 following Chapter 1.) If $x=0$ at $t=0$, a solution (as may be verified by substitution) is

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

This solution shows that the position of the particle varies *harmonically* (that is, as a sine function) with a frequency ν, and that the frequency is high for light particles (m small) attached to stiff springs (k_f large).

Self-test B.2 How does the momentum of the oscillator vary with time?

Answer: $p=2\pi\nu Am\cos(2\pi\nu t)$

To accelerate a rotation it is necessary to apply a **torque**, T, a twisting force. Newton's equation is then

$$\frac{dJ}{dt}=T \qquad \textit{Definition} \quad \text{Torque} \quad \text{(B.6)}$$

The analogous roles of m and I, of v and ω, and of p and J in the translational and rotational cases respectively should be remembered because they provide a ready way of constructing and recalling equations. These analogies are summarized in Table B.1.

Table B.1 Analogies between translation and rotation

Translation		Rotation	
Property	**Significance**	**Property**	**Significance**
Mass, m	Resistance to the effect of a force	Moment of inertia, I	Resistance to the effect of a torque
Speed, v	Rate of change of position	Angular velocity, ω	Rate of change of angle
Magnitude of linear momentum, p	$p=mv$	Magnitude of angular momentum, J	$J=I\omega$
Translational kinetic energy, E_k	$E_k=\frac{1}{2}mv^2$ $=p^2/2m$	Rotational kinetic energy, E_k	$E_k=\frac{1}{2}I\omega^2$ $=J^2/2I$
Equation of motion	$dp/dt=F$	Equation of motion	$dJ/dt=T$

B.2 Energy: a first look

Before defining the term 'energy', we need to develop another familiar concept, that of 'work', more formally. Then we preview the uses of these concepts in chemistry.

(a) Work

Work, w, is done in order to achieve motion against an opposing force. For an infinitesimal displacement through $d\boldsymbol{s}$ (a vector), the work done is

$$dw=-\boldsymbol{F}\cdot d\boldsymbol{s} \qquad \textit{Definition} \quad \text{Work} \quad \text{(B.7a)}$$

where $\boldsymbol{F}\cdot d\boldsymbol{s}$ is the 'scalar product' of the vectors $\boldsymbol{F}$ and $d\boldsymbol{s}$:

$$\boldsymbol{F}\cdot d\boldsymbol{s}=F_x dx+F_y dy+F_z dz \qquad \textit{Definition} \quad \text{Scalar product} \quad \text{(B.7b)}$$

For motion in one dimension, we write $dw=-F_x dx$. The total work done along a path is the integral of this expression, allowing for the possibility that $\boldsymbol{F}$ changes in direction and magnitude at each point of the path. With force in newtons and distance in metres, the units of work are joules (J), with

$$1\,\text{J}=1\,\text{N m}=1\,\text{kg m}^2\,\text{s}^{-2}$$

Brief illustration B.3 The work of stretching a bond

The work needed to stretch a chemical bond that behaves like a spring through an infinitesimal distance dx is

$$dw=-F_x dx=-(-k_f x)dx=k_f x dx$$

The total work needed to stretch the bond from zero displacement ($x=0$) at its equilibrium length R_e to a length R, corresponding to a displacement $x=R-R_e$, is

$$w=\int_0^{R-R_e} k_f x dx=k_f\int_0^{R-R_e} x dx=\tfrac{1}{2}k_f(R-R_e)^2$$

We see that the work required increases as the square of the displacement: it takes four times as much work to stretch a bond through 20 pm as it does to stretch the same bond through 10 pm.

Self-test B.3 The force constant of the H–H bond is about $575\,\text{N m}^{-1}$. How much work is needed to stretch this bond by 10 pm?

Answer: 28.8 zJ

(b) The definition of energy

Energy is the capacity to do work. The SI unit of energy is the same as that of work, namely the joule. The rate of supply of energy is called the **power** (P), and is expressed in watts (W):

$$1\,\mathrm{W} = 1\,\mathrm{J\,s^{-1}}$$

Calories (cal) and kilocalories (kcal) are still encountered in the chemical literature. The calorie is now defined in terms of the joule, with 1 cal=4.184 J (exactly). Caution needs to be exercised as there are several different kinds of calorie. The 'thermochemical calorie', cal$_{15}$, is the energy required to raise the temperature of 1 g of water at 15 °C by 1 °C and the 'dietary Calorie' is 1 kcal.

A particle may possess two kinds of energy, kinetic energy and potential energy. The **kinetic energy**, E_k, of a body is the energy the body possesses as a result of its motion. For a body of mass m travelling at a speed v,

$$E_k = \tfrac{1}{2}mv^2 \tag{B.8}$$

Definition Kinetic energy

It follows from Newton's second law that if a particle of mass m is initially stationary and is subjected to a constant force F for a time τ, then its speed increases from zero to $F\tau/m$ and therefore its kinetic energy increases from zero to

$$E_k = \frac{F^2\tau^2}{2m} \tag{B.9}$$

The energy of the particle remains at this value after the force ceases to act. Because the magnitude of the applied force, F, and the time, τ, for which it acts may be varied at will, eqn B.9 implies that the energy of the particle may be increased to any value.

The **potential energy**, E_p or V, of a body is the energy it possesses as a result of its position. Because (in the absence of losses) the work that a particle can do when it is stationary in a given location is equal to the work that had to be done to bring it there, we can use the one-dimensional version of eqn B.7 to write $dV=-F_x dx$, and therefore

$$F_x = -\frac{dV}{dx} \tag{B.10}$$

Definition Potential energy

No universal expression for the potential energy can be given because it depends on the type of force the body experiences. For a particle of mass m at an altitude h close to the surface of the Earth, the gravitational potential energy is

$$V(h) = V(0) + mgh \tag{B.11}$$

Gravitational potential energy

where g is the **acceleration of free fall** (g depends on location, but its 'standard value' is close to 9.81 m s^{-2}). The zero of potential energy is arbitrary. For a particle close to the surface of the Earth, it is common to set $V(0)=0$.

The **total energy** of a particle is the sum of its kinetic and potential energies:

$$E = E_k + E_p, \text{or } E = E_k + V \tag{B.12}$$

Definition Total energy

We make use of the apparently universal law of nature that *energy is conserved*; that is, energy can neither be created nor destroyed. Although energy can be transferred from one location to another and transformed from one form to another, the total energy is constant. In terms of the linear momentum, the total energy of a particle is

$$E = \frac{p^2}{2m} + V \tag{B.13}$$

This expression may be used in place of Newton's second law to calculate the trajectory of a particle.

Brief illustration B.4 The trajectory of a particle

Consider an argon atom free to move in one direction (along the x-axis) in a region where $V=0$ (so the energy is independent of position). Because $v=dx/dt$, it follows from eqns B.1 and B.8 that $dx/dt=(2E_k/m)^{1/2}$. As may be verified by substitution, a solution of this differential equation is

$$x(t) = x(0) + \left(\frac{2E_k}{m}\right)^{1/2} t$$

The linear momentum is

$$p(t) = mv(t) = m\frac{dx}{dt} = (2mE_k)^{1/2}$$

and is a constant. Hence, if we know the initial position and momentum, we can predict all later positions and momenta exactly.

Self-test B.4 Consider an atom of mass m moving along the x direction with an initial position x_1 and initial speed v_1. If the atom moves for a time interval Δt in a region where the potential energy varies as $V(x)$, what is its speed v_2 at position x_2?

Answer: $v_2 = v_1 \left|dV(x)/dx\right|_{x_1} \Delta t/m$

(c) The Coulomb potential energy

One of the most important kinds of potential energy in chemistry is the **Coulomb potential energy** between two electric charges. The Coulomb potential energy is equal to the work that must be done to bring up a charge from infinity to a distance r from a second charge. For a point charge Q_1 at a distance r in a vacuum from another point charge Q_2, their potential energy is

$$V(r)=\frac{Q_1Q_2}{4\pi\varepsilon_0 r} \qquad \textit{Definition} \qquad \text{Coulomb potential energy} \qquad \text{(B.14)}$$

Charge is expressed in coulombs (C), often as a multiple of the fundamental charge, e. Thus, the charge of an electron is $-e$ and that of a proton is $+e$; the charge of an ion is ze, with z the **charge number** (positive for cations, negative for anions). The constant ε_0 (epsilon zero) is the **vacuum permittivity**, a fundamental constant with the value $8.854\times10^{-12}\,\mathrm{C^2\,J^{-1}\,m^{-1}}$. It is conventional (as in eqn B.14) to set the potential energy equal to zero at infinite separation of charges. Then two opposite charges have a negative potential energy at finite separations whereas two like charges have a positive potential energy.

Brief illustration B.5 The Coulomb potential energy

The Coulomb potential energy resulting from the electrostatic interaction between a positively charged sodium cation, Na^+, and a negatively charged chloride anion, Cl^-, at a distance of 0.280 nm, which is the separation between ions in the lattice of a sodium chloride crystal, is

$$V=\frac{\overbrace{(-1.602\times10^{-19}\,\mathrm{C})}^{Q(\mathrm{Cl}^-)}\times\overbrace{(1.602\times10^{-19}\,\mathrm{C})}^{Q(\mathrm{Na}^+)}}{4\pi\times\underbrace{(8.854\times10^{-12}\,\mathrm{C^2\,J^{-1}\,m^{-1}})}_{\varepsilon_0}\times\underbrace{(0.280\times10^{-9}\,\mathrm{m})}_{r}}$$

$$=-8.24\times10^{-19}\,\mathrm{J}$$

This value is equivalent to a molar energy of

$$V\times N_{\mathrm{A}}=(-8.24\times10^{-19}\,\mathrm{J})\times(6.022\times10^{23}\,\mathrm{mol^{-1}})=-496\,\mathrm{kJ\,mol^{-1}}$$

A note on good practice: Write units at *every* stage of a calculation and do not simply attach them to a final numerical value. Also, it is often sensible to express all numerical quantities in scientific notation using exponential format rather than SI prefixes to denote powers of ten.

Self-test B.5: The centres of neighbouring cations and anions in magnesium oxide crystals are separated by 0.21 nm. Determine the molar Coulomb potential energy resulting from the electrostatic interaction between a Mg^{2+} and an O^{2-} ion in such a crystal.

Answer: $2600\,\mathrm{kJ\,mol^{-1}}$

In a medium other than a vacuum, the potential energy of interaction between two charges is reduced, and the vacuum permittivity is replaced by the **permittivity**, ε, of the medium. The permittivity is commonly expressed as a multiple of the vacuum permittivity:

$$\varepsilon=\varepsilon_{\mathrm{r}}\varepsilon_0 \qquad \textit{Definition} \qquad \text{Permittivity} \qquad \text{(B.15)}$$

with ε_{r} the dimensionless **relative permittivity** (formerly, the *dielectric constant*). This reduction in potential energy can be substantial: the relative permittivity of water at 25 °C is 80, so the reduction in potential energy for a given pair of charges at a fixed difference (with sufficient space between them for the water molecules to behave as a fluid) is by nearly two orders of magnitude.

Care should be taken to distinguish *potential energy* from *potential*. The potential energy of a charge Q_1 in the presence of another charge Q_2 can be expressed in terms of the **Coulomb potential**, ϕ (phi):

$$V(r)=Q_1\phi(r) \qquad \phi(r)=\frac{Q_2}{4\pi\varepsilon_0 r} \qquad \textit{Definition} \qquad \text{Coulomb potential} \qquad \text{(B.16)}$$

The units of potential are joules per coulomb, $\mathrm{J\,C^{-1}}$, so when ϕ is multiplied by a charge in coulombs, the result is in joules. The combination joules per coulomb occurs widely and is called a volt (V):

$$1\,\mathrm{V}=1\,\mathrm{J\,C^{-1}}$$

35289

If there are several charges $Q_2, Q_3, \ldots$ present in the system, the total potential experienced by the charge Q_1 is the sum of the potential generated by each charge:

$$\phi=\phi_2+\phi_3+\cdots \qquad \text{(B.17)}$$

Just as the potential energy of a charge Q_1 can be written $V=Q_1\phi$, so the magnitude of the force on Q_1 can be written $F=Q_1\mathcal{E}$, where $\mathcal{E}$ is the magnitude of the **electric field strength** (units: volts per metre, $\mathrm{V\,m^{-1}}$) arising from Q_2 or from some more general charge distribution. The electric field strength (which, like the force, is actually a vector quantity) is the negative gradient of the electric potential. In one dimension, we write the magnitude of the electric field strength as

$$\mathcal{E}=-\frac{\mathrm{d}\phi}{\mathrm{d}x} \qquad \text{Electric field strength} \qquad \text{(B.18)}$$

The language we have just developed inspires an important alternative energy unit, the **electronvolt** (eV): 1 eV is defined as the kinetic energy acquired when an electron is accelerated from rest through a potential difference of 1 V. The relation between electronvolts and joules is

$$1\,\mathrm{eV}=1.602\times10^{-19}\,\mathrm{J}$$

Many processes in chemistry involve energies of a few electronvolts. For example, to remove an electron from a sodium atom requires about 5 eV.

A particularly important way of supplying energy in chemistry (as in the everyday world) is by passing an electric current through a resistance. An **electric current** (I) is defined as the rate of supply of charge, $I=\mathrm{d}Q/\mathrm{d}t$, and is measured in *amperes* (A):

$$1\,\mathrm{A}=1\,\mathrm{C\,s^{-1}}$$

If a charge Q is transferred from a region of potential ϕ_i, where its potential energy is $Q\phi_i$, to where the potential is ϕ_f and its potential energy is $Q\phi_f$, and therefore through a potential difference $\Delta\phi=\phi_f-\phi_i$, the change in potential energy is $Q\Delta\phi$. The rate at which the energy changes is $(\mathrm{d}Q/\mathrm{d}t)\Delta\phi$, or $I\Delta\phi$. The power is therefore

$$P=I\Delta\phi \qquad \text{Electrical power} \tag{B.19}$$

With current in amperes and the potential difference in volts, the power is in watts. The total energy, E, supplied in an interval Δt is the power (the rate of energy supply) multiplied by the duration of the interval:

$$E=P\Delta t=I\Delta\phi\Delta t \tag{B.20}$$

The energy is obtained in joules with the current in amperes, the potential difference in volts, and the time in seconds.

(d) Thermodynamics

The systematic discussion of the transfer and transformation of energy in bulk matter is called **thermodynamics**. This subtle subject is treated in detail in the text, but it will be familiar from introductory chemistry that there are two central concepts, the **internal energy**, U (units: joules, J), and the **entropy**, S (units: joules per kelvin, $\mathrm{J\,K^{-1}}$).

The internal energy is the total energy of a system. The **First Law of thermodynamics** states that the internal energy is constant in a system isolated from external influences. The internal energy of a sample of matter increases as its temperature is raised, and we write

$$\Delta U=C\Delta T \qquad \text{Change in internal energy} \tag{B.21}$$

where ΔU is the change in internal energy when the temperature of the sample is raised by ΔT. The constant C is called the **heat capacity**, C (units: joules per kelvin, $\mathrm{J\,K^{-1}}$), of the sample. If the heat capacity is large, a small increase in temperature results in a large increase in internal energy. This remark can be expressed in a physically more significant way by inverting it: if the heat capacity is large, then even a large transfer of energy into the system leads to only a small rise in temperature. The heat capacity is an extensive property, and values for a substance are commonly reported as the **molar heat capacity**, $C_m=C/n$ (units: joules per kelvin per mole, $\mathrm{J\,K^{-1}\,mol^{-1}}$) or the **specific heat capacity**, $C_s=C/m$ (units: joules per kelvin per gram, $\mathrm{J\,K^{-1}\,g^{-1}}$), both of which are intensive properties.

Thermodynamic properties are often best discussed in terms of infinitesimal changes, in which case we would write eqn B.21 as $\mathrm{d}U=C\mathrm{d}T$. When this expression is written in the form

$$C=\frac{\mathrm{d}U}{\mathrm{d}T} \qquad \textit{Definition} \quad \text{Heat capacity} \tag{B.22}$$

we see that the heat capacity can be interpreted as the slope of the plot of the internal energy of a sample against the temperature.

As will also be familiar from introductory chemistry and will be explained in detail later, for systems maintained at constant pressure it is usually more convenient to modify the internal energy by adding to it the quantity pV, and introducing the **enthalpy**, H (units: joules, J):

$$H=U+pV \qquad \textit{Definition} \quad \text{Enthalpy} \tag{B.23}$$

The enthalpy, an extensive property, greatly simplifies the discussion of chemical reactions, in part because changes in enthalpy can be identified with the energy transferred as heat from a system maintained at constant pressure (as in common laboratory experiments).

Brief illustration B.6 The relation between U and H

The internal energy and enthalpy of a perfect gas, for which $pV=nRT$, are related by

$$H=U+nRT$$

Division by n and rearrangement gives

$$H_m-U_m=RT$$

where H_m and U_m are the molar enthalpy and the molar internal energy, respectively. We see that the difference between H_m and U_m increases with temperature.

Self-test B.6 By how much does the molar enthalpy of oxygen gas differ from its molar internal energy at 298 K?

Answer: $2.48\,\mathrm{kJ\,mol^{-1}}$

The **entropy**, S, is a measure of the *quality* of the energy of a system. If the energy is distributed over many modes of motion (for example, the rotational, vibrational, and translational motions for the particles that comprise the system), then the entropy is high. If the energy is distributed over only a small number of modes of motion, then the entropy is low. The **Second Law of thermodynamics** states that any spontaneous (that is, natural) change in an isolated system is accompanied by an increase in the entropy of the system. This tendency is commonly expressed by saying that the natural direction of change is accompanied by dispersal of energy from a localized region or its conversion to a less organized form.

The entropy of a system and its surroundings is of the greatest importance in chemistry because it enables us to identify the spontaneous direction of a chemical reaction and to identify the composition at which the reaction is at **equilibrium**. In a state of *dynamic* equilibrium, which is the character of all chemical equilibria, the forward and reverse reactions are occurring at the same rate and there is no net tendency to change in either direction. However, to use the entropy to identify this state we need to consider both the system and its surroundings. This task can be simplified if the reaction is taking place at constant temperature and pressure, for then it is possible to identify the state of equilibrium as the state at which the **Gibbs energy**, G (units: joules, J), of the system has reached a minimum. The Gibbs energy is defined as

$$G = H - TS \qquad \textit{Definition} \quad \text{Gibbs energy} \qquad \text{(B.24)}$$

and is of the greatest importance in chemical thermodynamics. The Gibbs energy, which informally is called the 'free energy', is a measure of the energy stored in a system that is free to do useful work, such as driving electrons through a circuit or causing a reaction to be driven in its nonspontaneous (unnatural) direction.

B.3 The relation between molecular and bulk properties

The energy of a molecule, atom, or subatomic particle that is confined to a region of space is **quantized**, or restricted to certain discrete values. These permitted energies are called **energy levels**. The values of the permitted energies depend on the characteristics of the particle (for instance, its mass) and the extent of the region to which it is confined. The quantization of energy is most important—in the sense that the allowed energies are widest apart—for particles of small mass confined to small regions of space. Consequently, quantization is very important for electrons in atoms and molecules, but usually unimportant for macroscopic bodies, for which the separation of translational energy levels of particles in containers of macroscopic dimensions is so small that for all practical purposes their translational motion is unquantized and can be varied virtually continuously.

The energy of a molecule other than its unquantized translational motion arises mostly from three modes of motion: rotation of the molecule as a whole, distortion of the molecule through vibration of its atoms, and the motion of electrons around nuclei. Quantization becomes increasingly important as we change focus from rotational to vibrational and then to electronic motion. The separation of rotational energy levels (in small molecules, about 10^{-21} J or 1 zJ, corresponding to about 0.6 kJ mol^{-1}) is smaller than that of vibrational energy levels (about 10 − 100 zJ, or 6 − 60 kJ mol^{-1}), which itself is smaller than that of electronic energy levels (about 10^{-18} J or 1 aJ, where a is another uncommon but useful SI prefix, standing for atto, 10^{-18}, corresponding to about 600 kJ mol^{-1}). Figure B.3 depicts these typical energy level separations.

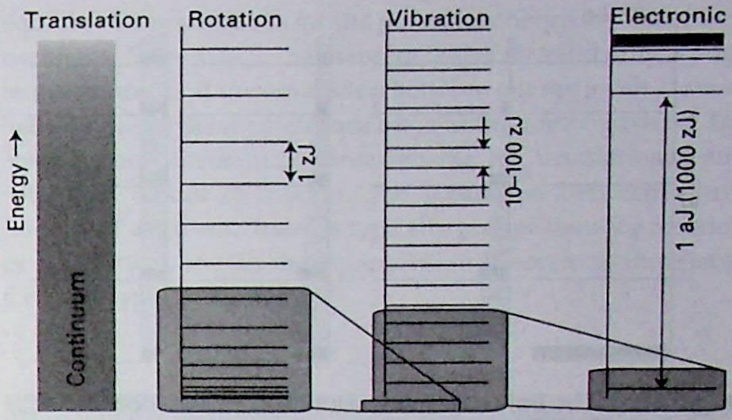

Figure B.3 The energy level separations typical of four types of system. (1 zJ = 10^{-21} J; in molar terms, 1 zJ is equivalent to about 0.6 kJ mol^{-1}.)

(a) The Boltzmann distribution

The continuous thermal agitation that the molecules experience in a sample at $T > 0$ ensures that they are distributed over the available energy levels. One particular molecule may be in a state corresponding to a low energy level at one instant, and then be excited into a high energy state a moment later. Although we cannot keep track of the state of a single molecule, we can speak of the *average* numbers of molecules in each state; even though individual molecules may be changing their states as a result of collisions, the average number in each state is constant (provided the temperature remains the same).

The average number of molecules in a state is called the **population** of the state. Only the lowest energy state is occupied at $T = 0$. Raising the temperature excites some molecules into higher energy states, and more and more states become accessible as the temperature is raised further (Fig. B.4). The formula for calculating the relative populations of states of various energies is called the **Boltzmann distribution** and was derived by the Austrian scientist Ludwig Boltzmann towards the end of the nineteenth century. This formula gives the ratio of the numbers of particles in states with energies ε_i and ε_j as

$$\frac{N_i}{N_j} = e^{-(\varepsilon_i - \varepsilon_j)/kT} \qquad \text{Boltzmann distribution} \qquad \text{(B.25a)}$$

where k is **Boltzmann's constant**, a fundamental constant with the value $k = 1.381 \times 10^{-23}$ J K^{-1}. In chemical applications it is common to use not the individual energies but energies per mole of molecules, E_i, with $E_i = N_A \varepsilon_i$, where N_A is Avogadro's