CHAPTER 1

Some Basic Ideas and Examples

1.1 INTRODUCTION

Physical chemistry is widely perceived as a collection of largely independent topics, few of which appear straightforward. This book aims to remove this misconception by basing it securely on the atoms and molecules that constitute matter, and their properties. We shall concentrate on just two aspects and we focus mainly on thermodynamics, which although extremely powerful is one of the least popular subjects with students. A briefer account describes how reactions occur. We shall nevertheless encounter the major building blocks of physical chemistry, the foundations that, if understood, together with their inter-dependence, remove any mystique. These include statistical thermodynamics, thermodynamics and quantum theory.

   The way that physical chemistry is taught today reflects the historical process by which understanding was initially obtained. One subject led to another, not necessarily with any underlying philosophical connection but largely as a result of what was possible at the time. All experiments involved very large numbers of molecules (although when thermodynamics was first formulated the existence of atoms and molecules was not generally accepted) and people attempted to decipher what happened at a molecular level from their results. This was very indirect. Nowadays the existence and properties of atoms and molecules are established and experiments can even be performed on individual atoms and molecules. This provides the opportunity for a different way of looking at the subject, building from these properties to deduce the characteristic behaviour of large collections of them, which is more in keeping with how chemistry is taught at school level. Similarly, our understanding of how reactions occur has come from observations of samples containing huge numbers of molecules and we have tried to deduce what happens at molecular level from them. Yet it is now possible to observe reactions between individual pairs of molecules, and we can reverse the procedure and start from these observations to understand

reactions in bulk. It is the object of this book to demonstrate the possibility of a molecular approach to thermodynamics and reaction dynamics. It is not intended as an introduction to these subjects but rather is offered as an aid to understanding them, with some prior knowledge assumed.

We start with the properties of atoms and molecules as deduced from thermodynamic measurements and from spectroscopy. This is, paradoxically, the historical approach but it establishes straightaway that the properties are directly connected to the thermodynamics and it is artificial to separate the two. But once the connection is established we show how it can be exploited to give real insight into various problems. In this chapter we introduce the fact that the energy levels of atoms and molecules are quantised and use some simple ideas to establish the effectiveness of our general approach before proceeding to their origins in the second chapter.

1.2 ENERGIES AND HEAT CAPACITIES OF ATOMS

In the gas phase, atoms move freely in space and frequently collide, at a rate that depends upon the pressure of the gas. At atmospheric pressure ($\sim 10^5$ N m^{-2}) and room temperature they move approximately 100 molecular diameters between collisions, at average velocities about equal to that of a rifle bullet (300 m s^{-1}). In elastic collisions some atoms effectively stop whilst others gain increased velocity (*cf.* collisions of billiard balls) so that instead of all the atoms having a single velocity they have a wide distribution of velocities. This is the familiar Maxwell distribution (Figure 1.1) that results from classical Newtonian mechanics. In it all velocities are possible but some are more probable than others. The most probable velocity depends upon the temperature, as does the width of the distribution.

A moving atom of mass m possesses a kinetic energy of $\frac{1}{2}mu^2$, where u is its velocity. Since in the whole collection of atoms in a gas there is no restriction to the velocity of an atom, there is no restriction to its energy either. Using the Maxwell distribution (see below), the average energy of an atom can be shown to be

$$\bar{\varepsilon} = \tfrac{1}{2}\, m\overline{u^2} = \tfrac{3}{2}kT \qquad (1.1)$$

where $\overline{u^2}$ is the mean square velocity of the atoms in the sample, k is Boltzmann's constant ($k = R/N_A$ where R is the universal gas constant and N_A the Avogadro number) and T is the absolute temperature. To obtain the total energy, E, of a mole of gas we simply multiply by the total number of atoms, N_A, and obtain $(\tfrac{3}{2})RT$. This is the energy due to the
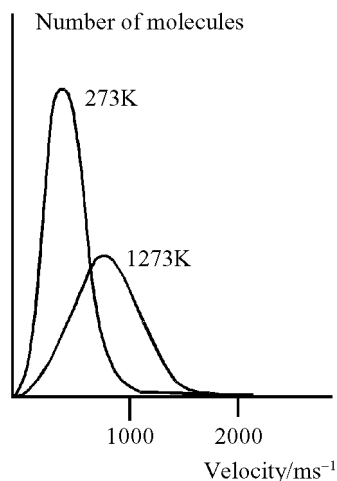
Figure 1.1 *The Maxwell distribution of velocities of molecules in a gas at 273 and 1273 K. As the temperature is increased the most probable velocity moves to a higher value and the distribution widens, reflecting a greater range of molecular velocities.*

motion (translation) of the atoms in the gas, the 'translational energy'.

Remarkably, although the kinetic energy of an individual atom depends upon its mass, the prediction is that the total energy of the gas in the sample does not. It seemed so outrageous when first made that it had to be tested, but how? We have calculated the absolute quantity, E, but have no way of measuring it directly. But there is a closely related property that we can measure. This is the heat capacity of the system, defined as the amount of heat required to raise the temperature of a given quantity of gas (here 1 mole) by 1 K. Different values are obtained if this measurement is made keeping the volume of the gas constant (with a heat capacity defined as C_V) or keeping its pressure constant (C_P) since in the latter case energy is expended in expanding the gas against external pressure. Here we consider just what is happening to the energy of the gas itself, and must use the former. Writing the definition in mathematical form, as a partial differential (a differential with respect to just one variable, here T),

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial(\frac{3}{2}RT)}{\partial T}\right)_V = \tfrac{3}{2}R = 12.47 \text{ J K}^{-1}\text{ mol}^{-1} \qquad (1.2)$$

The subscript on the bracket reminds us that we are dealing with a constant volume system.

This is again remarkable. It says that for all monatomic gases, regard-

less of their precise chemical nature or mass, the molar heat capacity is the same, and independent of temperature. Experiment shows this to be correct. For example, He, Ne, Ar and Kr were early shown to have precisely this value over the temperature range 173–873 K, the range then investigated.

It is now worth examining in more detail where the result that the mean energy of a monatomic gas is independent of its nature comes from. To obtain this average over the whole range of velocities we must multiply the kinetic energy of an atom at a given velocity by the probability that it has this velocity, and integrate over the whole velocity distribution normalised to the total number of atoms present. This probability function ($\mathrm{d}N/N$) is the Maxwell distribution of velocities.

$$E = \tfrac{1}{2}\,m\overline{u^2} = \int\limits_0^\infty \tfrac{1}{2}\,mu^2\,\frac{\mathrm{d}N}{N} \tag{1.3}$$

where

$$\frac{\mathrm{d}N}{N} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{-mu^2}{2kT}\right)u^2\mathrm{d}u \tag{1.4}$$

Thus the expression for E, clearly and understandably, contains the mass, m, and the velocity, u. Yet due to its mathematical form and since the integral is real (and is evaluated between these upper and lower limits) its value ($\tfrac{3}{2}kT$ for motion in three dimensions, Equation 1.1) does not. The expression may look formidable but the integral has a standard form (it is a *Gaussian* function) and its evaluation is straightforward; see Appendix 1.1. It follows that the same result is obtained for any form of energy (not necessarily translational) that can be expressed in the same mathematical form, $\tfrac{1}{2}ab^2$, where 'a' is a constant and 'b' is a variable that can take any value within a Maxwellian distribution. Such a term is known as a 'squared term'.

From experience, gases are homogeneous and possess the same properties in all three directions in space; for example, the pressure is the same in all directions. The motion of the gas atoms in the three perpendicular Cartesian directions is independent and we say that they have three 'translational degrees of freedom'. Resolving the velocity into these directions and using Pythagoras gives, with obvious notation,

$$u^2 = u_x^2 + u_y^2 + u_z^2 \tag{1.5}$$

with an analogous result for their means. In the gas the mean square velocities in the three directions are equal. The form of the Maxwell

distribution we have used is that for motion in three dimensions and the average energy associated with each translational degree of freedom is consequently one-third of the value obtained. It then follows that for each degree of freedom *whose energy can be expressed as a squared term* we should expect an average energy of $\frac{1}{2}kT$ per atom. This is an important result of classical physics and is the quantitative statement of 'the Principle of the Equipartition of Energy'.

We stress that it has resulted from the Maxwell distribution in which there is no restriction of the translational energy that an atom (or molecule) can possess. From everyday experience this seems eminently reasonable. We can indeed make a car travel at a continuous range of velocities without restriction (and luckily personal choice of how hard we press the accelerator rather than collisions make a whole range possible if we consider a large number of cars!). But is this true of molecules that might possess other sources of energy besides translation? We should not assume so, but again put it to experimental test. We shall find later that we have to re-examine the case of translational energy too.

1.3 HEAT CAPACITIES OF DIATOMIC MOLECULES

The heat capacity, C_V, of a sample is directly related to its energy, and can be measured. We expect gaseous diatomic molecules, like atoms, to move freely in independent directions in space so that translational energy should confer upon the sample a heat capacity of $\frac{3}{2}R = 12.47$ J mol^{-1} K^{-1}. If this was the only source of energy that molecules possess then the heat capacity should have this value, and be independent of temperature. This turns out to be wrong on both counts. For example, the measured heat capacities (in J mol^{-1} K^{-1}) of dihydrogen and dichlorine at various temperatures are given in Table 1.1.

All these values are substantially greater than expected from translational motion. Through the direct relationship between C_V and E this implies that there must be additional contributions to the energy of the sample. We note also that for each gas the value increases with temperature, with a tendency for it to become constant at high temperatures for

Table 1.1 *Heat capacities (J mol^{-1} K^{-1}) of dihydrogen and dichlorines at different temperatures*

Molecule	298	400	600	800	1000
			$T(K)$		
H_2	20.52	20.87	21.01	21.30	21.89
Cl_2	25.53	26.49	28.29	28.89	29.10

dichlorine, and that over the whole range of temperatures in the table the heat capacity of dichlorine exceeds that of dihydrogen.

So what forms of energy can a diatomic molecule have that an atom cannot? The obvious physical difference is that in the molecule the centre of mass is no longer centred on the atoms. This implies that if there are internal motions in the molecule as it translates through space these have associated energies. The first, and most obvious, possibility is that the molecule might rotate. A sample containing rotating molecules might therefore possess both translational and rotational energy, and we need to assess the latter. The simplest, and quite good, model for molecular rotation is to treat the diatomic molecule as a rigid rotor (Figure 1.2) with the atoms as point masses (m_1 and m_2) separated from the centre of mass of the molecule by distances r_1 and r_2. Classical physics shows the rotational energy to be $\frac{1}{2}I\omega^2$, where I is its moment of inertia and ω the angular velocity (measured in rad s^{-1}). We immediately recognise this as a 'squared term'.

Rotation might occur about any of three independent axes which in general might have different moments of inertia, although for a diatomic molecule two are equal. Taking the bond as one axis (z), these are those about axes perpendicular to it through the centre of mass and their moments of inertia are defined by
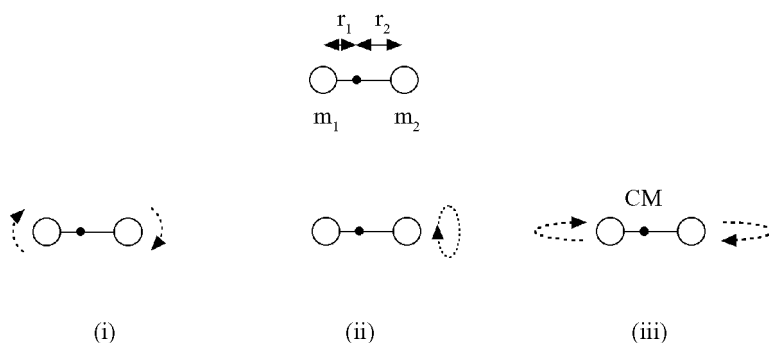
$$I_x = I_y = m_1 r_1^2 + m_2 r_2^2 \tag{1.6}$$

Figure 1.2 *Rotations of a diatomic molecule. The atoms are treated as point masses, m_1 and m_2, with their centres lying along the axis of the molecule with the distances r_1 and r_2 measured between these centres and the centre of mass (CM) of the molecule. The molecule can rotate about three axes, in the plane of the paper (i), about the bond axis (ii) and out of the plane (iii). The moments of inertia for rotations (i) and (iii) are non-zero and equal but the moment of inertia for rotation (ii) is zero since there is no perpendicular distance between the point masses and the CM along the bond axis. This rotation therefore does not contribute to the total rotational energy of the molecule.*

We note that the distances are measured in the direction perpendicular to the axes of rotation, here along the z-axis. This implies that the moment of inertia for rotation about the z-axis is zero because the point masses and the centre of mass all lie on a straight line, and no perpendicular distance in the x or y directions separates them. We conclude that only two of the three rotational degrees of freedom contribute to the energy of the molecule, both through squared terms in the angular velocity. Using the Equipartition Principle we predict that their contribution to the energy will be $2 \times \frac{1}{2}RT$ J mol^{-1}. This implies that, together with the translational contribution, the total energy of the molecule should be $\frac{5}{2}RT$ J mol^{-1} and C_V should be $\frac{5}{2}R$ J mol^{-1} K^{-1}. It should not vary as the temperature is changed.

This has the value 20.78 J mol^{-1} K^{-1}, which, interestingly and significantly (see later), is very close to the value observed for dihydrogen at 350 K, but Table 1.1 shows C_V to increase with temperature. However, for dichlorine it is still much too low at this temperature compared with experiment. Once again we conclude that the actual energy is greater than we thought, and that the molecule must have another form of internal motion associated with it. This is vibration.

In a vibration the atoms continuously move in and out about their average positions (Figure 1.3). As they move outwards the bond is stretched, as would be a spring, and this generates a restoring force, which
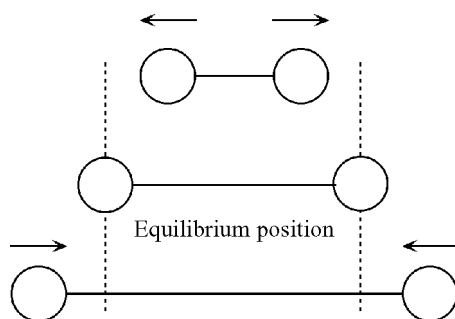

Figure 1.3 *Vibration of a diatomic molecule. The diagram shows at the top the (point mass) atoms at their distance of closest approach when they start to move apart again, in the centre at their average positions, and at the bottom when the bond is fullest stretched and the elasticity of the bond brings the atoms back towards each other once more. At the two extreme positions the atoms are momentarily stationary and the molecule possesses the potential energy obtained from stretching or compressing the bond only, but they then start to move, transforming potential energy into kinetic energy, a process complete just as the atoms pass through their equilibrium positions. If the bond stretching obeys Hooke's Law (the restoring force generated by moving away from the equilibrium position is proportional to the distance moved) then Simple Harmonic Motion results.*

if Hooke's Law is obeyed is proportional to the displacement from the equilibrium positions, and the atoms return through these positions. In this model (also quite good) the molecule behaves as a simple harmonic oscillator with continually interchanging kinetic (KE, from the motion of the atoms) and potential (PE, from stretching the bond) energies. The total energy is the sum of the two, and is conserved in an isolated gas molecule.

$$E_{vib} = (KE + PE)_{vib} \qquad (1.7)$$

At any instant the kinetic energy is given classically by $\frac{1}{2}\mu v^2$ where μ is the 'reduced mass' of the molecule (defined as $m_1 m_2/(m_1 + m_2)$) and v is the instantaneous velocity of the atoms, whilst the potential energy is $\frac{1}{2}kx^2$, where k is the bond force constant (Hooke's Law constant) and x is the instantaneous displacement from the average position of each atom. A diatomic molecule can only vibrate in one way, in the direction of the bond, but because of having to sum the contributions from both forms of energy this one degree of vibrational freedom contributes two squared terms to the total energy, through the Equipartition Principle, $2 \times \frac{1}{2}RT$ J mol^{-1}. Once again we have assumed that, in using this Principle, there are no limitations on (now) the vibrational energy that a molecule can possess.

The total energy of the molecule is, therefore, predicted to be the sum of the translational ($\frac{3}{2}RT$), rotational (RT) and vibrational (RT) contributions, giving $\frac{7}{2}RT$ J mol^{-1} and $C_V = \frac{7}{2}R = 29.1$ J mol^{-1} K^{-1}, greater than before but still independent of temperature. This is precisely the value obtained experimentally for dichlorine at 1000 K but it is much higher than that of dihydrogen at the same temperature. The heat capacities of both are still predicted, wrongly, to be independent of temperature.

It is now instructive to plot C_V against T for a diatomic molecule (shown diagrammatically in Figure 1.4). The value jumps discontinuously between the three calculated values, corresponding to translation alone, translation plus rotation and finally translation plus rotation plus vibration, over small temperature ranges (near the characteristic temperatures for rotation and vibration, θ_{rot} and θ_{vib}, Section 2.5.1). These temperatures depend on the precise gas studied, and the changes occur at higher temperatures for molecules consisting of light atoms than for those that contain heavy ones. Only at the highest temperatures are the values those predicted by Equipartition. But the contribution from translation alone is evident at temperatures close to absolute zero, but not extremely close to it when this contribution falls to zero. In this plot the translational contribution is easily recognised through its unique value but which of
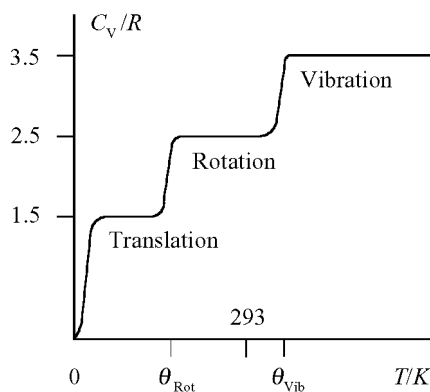
Figure 1.4 *Schematic diagram of how C_V for a diatomic molecule varies with temperature. It rises sharply from near 0 K and soon reaches $3R/2$, expected for translational motion, where it remains until a higher temperature (near θ_{rot}) is reached when the rotational degrees of freedom contribute another R to the overall value. This happens well below room temperature (293 K) for all diatomic molecules. At still higher temperatures the vibrational motion eventually contributes another R, again near a rather well-defined temperature (θ_{vib}). The actual values of these temperatures vary with the precise molecule concerned, and are lower for heavy molecules (e.g. Cl_2) than light ones (e.g. H_2). The beginnings of the vibrational contribution occur below room temperature for Cl_2 but the full contribution is not apparent until well above it.*

rotation or vibration contributes at the lower temperature is obtainable only through further experiment or theory; the rotational contribution appears at the lower temperature.

We conclude that molecules exhibit very different behaviour from that we predicted using classical theory and we must examine where we might have gone wrong. All the basic equations for rotational and vibrational energy are well established in classical physics and are not assumptions. One possibility might be that the rotational and vibrational energies are correctly given classically but that they do not have Maxwellian distributions. But also we have made what in the classical world seems a wholly unexceptional assumption, *i.e.* that there are no restrictions as to the energies a molecule might possess in its different degrees of freedom. Since the predictions do not conform to the experimental observations *this might be wrong*. We speculate that rather than being able to possess *any* values of their rotational and vibrational energies, the molecule may be able to possess *only specific values* of them. This is confirmed directly by spectroscopy, see below. We describe the energies as 'quantised'. This is the basic realisation from which much of physical chemistry flows.

Translational energy seems not to be quantised but actually is; experiments have to be performed at very close to 0 K to observe this. It is why

C_V in Figure 1.4 goes to zero at this temperature. The fact that different diatomic molecules possess the two further forms of energy above characteristic temperatures that differ from one molecule to the next is an aspect of energy-quantised systems that we shall have to understand. But all systems behave classically at high enough temperatures, which may, however, be below room temperature. For example, all diatomics (save H_2) exhibit their full rotational contribution below room temperature. But only the heaviest molecules exhibit the full vibrational contribution below very high temperatures.

That the limiting classical behaviour is often observed in real systems, especially for polyatomic molecules, is ultimately why we are normally unaware of the quantised nature of the world that surrounds us. But the world is quantised in energy and we need to understand and exploit the properties of matter that this implies. Much of the new technology in everyday use depends on it.

It is fascinating and significant that this conclusion of paramount importance was indicated as a possibility through the interpretation of classical thermodynamic measurements, emphasising that a connection exists between the thermodynamics of systems and the properties of the individual atoms and molecules that comprise them.

1.4   SPECTROSCOPY AND QUANTISATION

Quantisation of energy shows itself very directly in the optical spectra of atoms and molecules and initially we consider the electronic spectra of atoms. When a sample of atoms is excited in a flame, for example, it emits radiation to yield a 'line spectrum' (Figure 1.5). This is in fact a series of images of the exit slit in a spectrometer corresponding to a series of different discrete frequencies of light emitted by the atoms. If the atom behaved classically this would not be so since the electrostatic attraction between the electron and nucleus would accelerate one towards the other, and according to classical physical laws the atom would emit light over a continuous frequency range until the electron was annihilated on encountering the nucleus. The explanation is that the energies possible for the electrons in an atom are themselves quantised, and the frequencies in the emission spectrum correspond to the electron jumping between levels of different energy, according to the Bohr condition,

$$h v = E_1 - E_2 \tag{1.8}$$

where h is Planck's constant, v the frequency of the light and E_1 and E_2 are the energies of two of the levels (Figure 1.6).
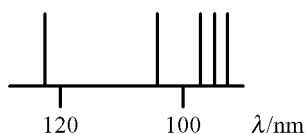
Figure 1.5 *Ultraviolet region of the emission spectrum of hydrogen atoms (the Lyman series). Atoms in the sample have been excited by an electric discharge to a number of higher atomic energy levels and they emit light at different discrete frequencies as the electrons return to the lowest level (principle quantum number, n=1). This displays the quantised nature of the atomic energy levels directly. Other series of lines are observed in the visible and infrared regions of the electromagnetic spectrum, corresponding to electron jumps to different lower quantised states. The positions of the lines allow the frequencies of the emitted light to be measured.*
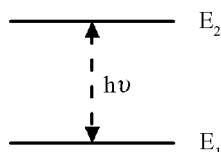

Figure 1.6 *The origin of a line in a spectrum of frequency v. In a H atom at thermal equilibrium with its surroundings the electron is in the lower energy level and it can absorb the specific amount of energy hv to jump to a higher energy level. If, however, the atom has been excited so as to put the electron in the upper energy level then it can emit the same energy and return to the lower level. In a real atom there are many pairs of energy levels between which spectroscopic transitions can occur.*

An early triumph of the Schrödinger equation was that it rationalised why the levels are quantised and allowed the energies to be calculated, with the difference frequencies agreeing with the observed ones. Associated with each level is a mathematical function, the wave function, known as an orbital.

The C_V measurements discussed above gave no indication that monatomic gases could possess electronic energy besides translational energy. This must mean that *over the temperature range studied* the atoms do not have any. But we have seen in Figure 1.4 that different sources of energy make their contributions at different temperatures and at a high enough temperature there would indeed be an electronic contribution to the C_V of atoms. We shall see later that the crucial factor is the energy separation between the quantised energy levels compared with the 'thermal energy' (given by kT) in the system, and the lower atomic orbitals are separated from each other by large energy gaps. For some atoms, such as the halogens (see below) an electronic contribution is evident even at quite low temperatures, but this is rather unusual.

In molecules, too, discrete energy levels and molecular orbitals exist with differing electronic energies. But associated with each and every

electronic level there is a set of vibrational and rotational ones (Figure 1.7). Through the Bohr condition spectroscopy allows us to measure the energy gaps directly, whilst quantum mechanics also allows us to calculate the energy levels, and the gaps between them. This confirms that the energies molecules possess are quantised. Molecular spectra are normally observed in absorption, with the molecules absorbing certain frequencies from white light flooding through a sample of them. Whereas emission spectra arise when electrons fall from higher energy levels into which the substance has been excited by heat or electricity, absorption spectra depend on species in their lower energy levels jumping to higher ones. They therefore give information on the lowest energy levels of the molecules. Experimentally a huge range of transition frequencies is involved, varying from the microwave (far infrared) to the ultraviolet regions of the electromagnetic spectrum. The former occur between energy levels that are closest in energy, those due to rotation. At higher frequencies, in the infrared, the light has sufficient energy to cause jumps between vibrational levels, but these all have more closely spaced associated rotational ones, and under certain selection rules changes occur to both the vibrational and rotational energies simultaneously. The spectra are known as 'vibration–rotation' ones (an example is given in Figure 2.6, Chapter 2). Finally, at much higher frequencies, in the ultraviolet, electrons can jump between the vibrational and rotational levels of different electronic energy states and the spectra reflect simultaneous changes in all three types of energy.

Through Equation (1.8) there is a direct relationship between frequency and energy difference and we conclude that *in terms of the gaps between the energy levels*

$$\Delta E(\text{electronic}) \gg \Delta E(\text{vibration}) > \Delta E(\text{rotation})(\text{and} \gg \Delta E(\text{translation})) \quad (1.9)$$

This confirms our conclusions from C_V measurements (Figure 1.4). At 0 K C_V is zero, but as the temperature is increased translational motion rapidly makes the contribution expected from classical physics. At a higher temperature the effects of rotation become apparent, and at a higher one still, vibration (and at very high temperatures electronic energy contributions might appear if dissociation does not take place first). *Motions corresponding to the lower energy gaps make their contributions at lower temperatures than those with higher energy gaps.*

It is important to distinguish between the absolute values of the various types of energy and the separations between the energy levels. Thus the gaps between translational levels are miniscule but even at very low temperature there is a contribution of $(\frac{3}{2})RT$ J mol^{-1} to the energy.
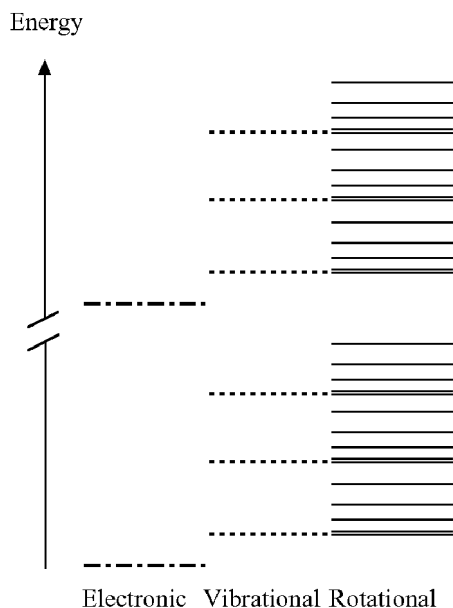
Figure 1.7 *Schematic diagram of the energy levels of a diatomic molecule showing only the two lowest electronic levels, which are widely separated in energy. Associated with each is a stack of more closely spaced vibrational levels, which in turn embrace a series of rotational levels. Under the Simple Harmonic oscillator approximation, the vibrational levels of each electronic level are equally spaced, but the rotational levels predicted by the rigid rotor model are not. This diagram gives an impression of the relative sizes of the electronic, vibrational and rotational energies but only a very few of the lower energy levels can be shown here without loss of clarity. Real molecules have far more levels. Spectroscopic transitions can be excited between the rotational levels alone, between the rotational levels in different vibrational states and between the sub-levels of the electronic energy states. The three types occur with very different energies and are observed in quite different regions of the electromagnetic spectrum.*

The gaps between electronic energy levels are enormous in comparison, yet electronic energy makes no contribution to the total energy of most systems at room temperature. A common error is to believe that since the energies of molecular electronic levels may be high then the electronic energy of the system must be high. If the molecule existed in one of the higher levels the energy would indeed be high. But it does not at low temperatures, where the molecule is in its lowest electronic level. For a gas at room temperature the translational energy is greatest in magnitude followed by the rotational energy and then the vibrational one. The order is exactly reversed from that of the energy gaps:

$$E(\text{translational}) > E(\text{rotational}) > E(\text{vibrational}) \, (\gg E(\text{electronic})) \quad (1.10)$$

1.5   SUMMARY

Atoms and molecules may possess several different contributions to their total energy but each one can have only certain discrete quantised values. The energies associated with different modes of motion differ in magnitude, with the gaps between the energy levels for translation being smaller than those for rotation that, in turn, are smaller than those for vibration. The gaps between the electronic energy levels of molecules normally vastly exceed all of these. This causes translational motion to occur at lower temperatures than rotational motion, which occurs at lower temperatures than vibration (and much lower than electronic excitation). Yet we remain unaware of quantisation in every day life, and we have some indication already that this is inherently because systems behave classically at high enough temperatures. We need to sharpen this concept and decide what a 'high enough' temperature is, and then we should be able to predict the behaviour of systems from a knowledge of the quantised energy levels of the atoms and molecules from which they are made.

1.6   FURTHER IMPLICATIONS FROM SPECTROSCOPY

We are so familiar today with spectra that we tend to miss a very remarkable fact about them. An atomic spectroscopic transition in absorption, for example, occurs when an atom in a specific energy level accepts energy from the radiation and jumps to another specific level, in accordance with the Bohr condition and under various selection rules that limit the transitions that are possible. These have been discovered by experiment, and can be rationalised using quantum mechanics. So the spectrum of a single atom undergoing a single transition is a single line at one specific frequency. But when we talk about the spectrum of an atom (a loose term) we immediately think of a whole family of transitions at different frequencies (Figure 1.5). Since the electron in one atom can only make one jump between energy levels at a time it follows that what we see is the result of a *large number* of individual atoms simultaneously absorbing energy and jumping to a whole range of possible quantum states. That is, instead of seeing the spectrum of a single atom, we are observing the spectra of a very large number of individual atoms simultaneously. We say that spectroscopy is an *ensemble phenomenon*, meaning precisely that what we observe is the result of what is happening in the large collection of atoms.

   But what would happen if we were clever enough to observe a single atom over a long period of time, rather than instantaneously? Following the initial absorption of energy from the light beam, the atom enters a

higher energy level. Let us now postulate that an efficient mechanism exists (it does!) for returning it to the lowest level, where it might absorb a different frequency from the incident radiation and attain a second, different, higher level. It would then return and the process be repeated over a whole cycle of possible transitions covering the total range of frequencies. We conclude that over infinite time the atom would perform all the possible transitions allowed to it and the spectrum of the single atom would be identical in appearance to the ensemble one. This has been put to direct experimental test in recent years, although in molecular rather than atomic spectroscopy, and found to be correct. It opens the possibility of calculating ensemble behaviour of a collection of molecules from the behaviour over time of a single one, a concept close to the basis of using ensembles in statistical thermodynamics (see later).

Another unexpected aspect of spectroscopy lies in the Bohr condition. We tend to think of atoms or molecules absorbing energy from an incident light beam and jumping to higher energy states, but Equation (1.8) does not dictate a direction for the energy change to occur. That is, whilst an atom in a lower energy state might jump to a higher energy state, one in that state might emit energy under the influence of the light beam, and fall back to the lower state. In this case the beam would exit more intense than it arrived. These processes are known as *stimulated absorption* and *stimulated emission* respectively. Einstein was the first to consider this and showed by a simple kinetic argument (it is now more satisfyingly done using quantum mechanics) that the absolute probability of an upward or a downward transition caused by light of the correct frequency is exactly the same. It follows that if there are molecules in both energy levels then the intensity of a spectroscopic line depends on the difference between the number of atoms that absorb energy from the light beam and those that emit energy to it, and therefore on the *difference* in the populations of the two energy levels. This is further considered in Section 4.4. So not only can spectroscopy measure the energy gaps in atoms and molecules, but it indicates this difference in populations, too.

Since all atoms and molecules at thermal equilibrium with their surroundings are found experimentally to exhibit absorption spectra, we conclude that *at thermal equilibrium* the lower energy states are the more highly populated. Samples in which the atoms are deliberately excited to higher levels, for example, by an electric discharge through them, have their upper levels overpopulated and exhibit emission spectra. This is how streets are lighted, using the emission spectrum of sodium. We should always remember that systems are not necessarily at thermal equilibrium; indeed, equilibrium can be disturbed or avoided in many ways of increasing technical importance. For example, lasers depend on

deliberately producing overpopulations of higher energy states.

1.7   NATURE OF QUANTISED SYSTEMS

The quantised world is a strange and un-instinctive one, complicated by the fact that polyatomic molecules possess millions of discrete energy levels. But we can understand what quantisation implies by studying it at its simplest and we initially consider a system that has just two energy levels available to it. That is, one in which the energy cannot vary without restriction, as in the classical physical world, but in which the atoms, molecules, nuclei or whatever that comprise the system can individually adopt one of just two possible energy states. Such systems actually exist. For example, the nucleus of the hydrogen atom, the proton, is magnetic and can interact with an applied magnetic field to affect its energy. Experiment shows that it is a quantum species whose magnetic moment can adopt either of two orientations with respect to the field direction, rather than the one that a classical compass needle would. In one orientation the magnetic moment lies along the direction of the applied field, and its energy is lowered, whilst in the other it opposes it, and its energy is increased. These are simple experimental facts and they imply that application of the field creates a two-level system [Figure 1.8(i)]. This is exploited in Nuclear Magnetic Resonance (NMR) spectroscopy, in which transitions are excited between the two levels. A different example is found in the halogen atoms that behave as though they were two-level systems at low temperature.

Let us be clear what is implied by the existence of the two levels. We define the energy of the lower to be 0, and that of the upper one ε. If we have one particle (an atom, a nucleus or whatever) in its lowest level its energy is 0, whereas if, somehow, we put it into the upper state its energy is ε. It is crucial to our understanding of quantised systems that *there is no other possibility*. The particle cannot, for example, have an energy of $\varepsilon/2$ or 1.2ε. This seems at odds with everyday life in which, up to some limit, systems seem to be able to possess any energy. For example, we can heat a kettle to any temperature below the boiling point of water. We need somehow to reconcile this difference with the classical world since we know that at atomic or molecular level *all* energies are quantised.

The secret once more lies in the fact that in the experiments we usually perform we do not study individual particles but rather collections of them in which they may be distributed between the two energy states. We start by simply adding a second [Figure 1.8(ii)]. Now both may be in the same energy level, to give a total energy of 0 or 2ε or one may be in one
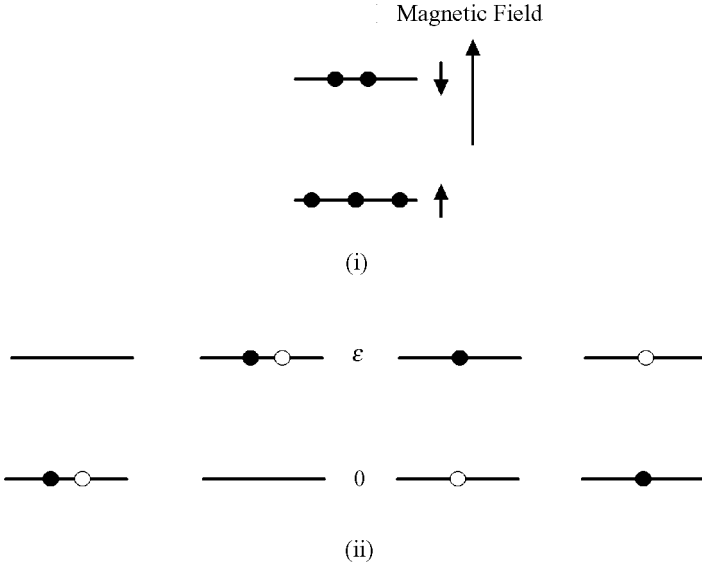
Figure 1.8 (i) *A two-level system results when hydrogen nuclei are placed inside a magnetic field. Some protons align with their magnetic moments along the applied field, and some against it, resulting in two different energy states. At thermal equilibrium there are more nuclei in the lower energy state than in the upper one. Nuclear Magnetic Resonance Spectroscopy consists in causing a transition between the two.* (ii) *If just two particles enter a two-level system their total energies can be 0, 2ε or ε, but if they enter the levels with equal probability then the latter can be obtained in two ways, unlike 0 and 2ε which can be obtained in just one.*

level and the other in the other, giving a total of ε. Now consider the *average* energy of the two. For this latter case this is ε/2, so that we now have an energy that is not one of the quantised values. The *total* energy is simply the number of particles times the average value (2 × ε/2), and in this case has a value equal to that of one of the quantised levels. But this is rarely true as we increase the number of particles in the system. Consider one in which there are $(m + n)$ particles divided between the two energy states, with m in the lower energy one. Now the total energy is $n\varepsilon$, which can take a range of values determined by n, and the average energy

$$\bar{E} = \frac{n\varepsilon}{(m + n)} \tag{1.11}$$

which is determined by the values of m and n. Whereas the energies of the individual particles have discrete, quantised, magnitudes, the average energy, and the total energy, have no such restrictions and can take a wide range of values. This lies at the heart of why systems containing

species with quantised energy levels nevertheless display classical behaviour under most conditions. These energies clearly depend on how the particles are distributed over the two energy states, that is on the numbers m and n.

This simple example leads to a further important insight. If we can distinguish between the particles, *i.e.* know which is which, then the situations with 0 or 2ε in total energy can each be obtained in just one way. But an energy of ε is obtained if either is in the lower level and the other in the upper one, in two ways. If both levels are equally likely to be populated this energy is twice as likely to occur as either of the others. Generalising, this implies that some population distributions and some energy values are more likely to occur than others. This is a conclusion of momentous importance. However, we stress that it depends on the likelihood of populating each level being inherently equal.

We shall now consider systems containing a large number of, *e.g.* molecules, which may exist in any of a large number of energy levels, before returning to the two-level system.

1.7.1 Boltzmann Distribution

Within chemistry we habitually deal with systems that contain a very large number (N) of molecules and we consider how these are distributed between their numerous energy levels when the systems are in thermal equilibrium with their surroundings at temperature T. For example, 1 mole of gas at 1 bar pressure contains N_A (6.022×10^{23}) molecules. We need the quantum analogue of the Maxwell distribution of energies. It is given by the Boltzmann distribution, which we shall state and use here before deriving it in Chapter 2. It is a statistical law that applies to a constant number of independent non-interacting molecules in a fixed volume, and is subject to the total energy of the system being constant (the system is isolated), and the several ways of obtaining this energy by distributing the molecules between the quantised levels being equally likely. That is, it does not matter which particular molecules are in specific energy states provided that the total energy is constant. The distribution is

$$\frac{n_i}{N} = \frac{g_i e^{-\varepsilon_i/kT}}{\sum_i g_i e^{-\varepsilon_i/kT}} \tag{1.12}$$

where n_i is the number of molecules in a level of energy ε_i and g_i is the degeneracy of that level (the number of states of equal energy, for

example, the three p orbitals of a H atom have the same energy and so for this $g_i = 3$). The denominator includes summation over all the energy levels of the molecules. This equation results from statistical theory applied to a very large number of molecules, under which conditions one particular distribution of the molecules between the quantised levels becomes so much more likely than the rest that it alone need be considered. This is the ultimate extension of our conclusion concerning just two levels.

On first encounter, the Boltzmann distribution looks formidable, especially because it apparently involves summation over the millions of energy levels present in polyatomic molecules. But we now return to the two-level system to discover the circumstances where this is only an apparent difficulty.

1.7.2 Two-level Systems

Consider a two-level system in which there are n_0 particles (atoms, molecules or whatever) in the lower level and n_1 in the upper one so that the total number $N = (n_0 + n_1)$. At thermal equilibrium the Boltzmann distribution tells us that these are related through

$$\frac{n_1}{(n_0 + n_1)} = \frac{g_1 e^{-\varepsilon/kT}}{g_0 e^{-0/kT} + g_1 e^{-\varepsilon/kT}} = \frac{g_1 e^{-\varepsilon/kT}}{g_0 + g_1 e^{-\varepsilon/kT}} \tag{1.13}$$

Rearrangement yields

$$\frac{n_1}{n_0} = \frac{g_1}{g_0} e^{-\varepsilon/kT} \tag{1.14}$$

In the simplest case the degeneracy of each state is 1, *e.g.* for protons inside a magnetic field. Here the ratio of the populations depends directly and solely on the value of the dimensionless exponent (ε/kT) that varies as the temperature is changed, ε being a fixed characteristic of the system. The denominator, kT, is known as the 'thermal energy' of the system. This energy is always freely available to us in systems at thermal equilibrium with their surroundings and, indeed, we cannot avoid it without decreasing the temperature to 0 K. This gives us a simple physical picture. The thermal energy is what a system possesses by virtue of the motion of the particles that comprise it, and we see that it is closely related, for example, to the mean thermal energy due to translation $\frac{3}{2}kT$, above. But the distribution tells us that in quantised systems we must compare kT to ε rather than $\frac{3}{2}$ times it. If kT is much less than ε we do not have the energy

to raise the particle from its lower energy level to the higher one, but as the temperature is increased it becomes possible to do so.

So much for the basic picture; now let us investigate the distribution semi-quantitatively. At low temperatures $kT \ll \varepsilon$ and for the sake of argument we let $kT = 10^{-4}\,\varepsilon$ so that $(\varepsilon/kT) = 10^4$. Now,

$$\frac{n_1}{n_0} = e^{-10000} \approx 0 \qquad (1.15)$$

As expected there are essentially no particles in the upper level. Now we increase the temperature to make $kT = \varepsilon$ so that $(\varepsilon/kT) = 1$, giving

$$\frac{n_1}{n_0} = e^{-1} \approx 0.37 \qquad (1.16)$$

and now many of the particles are in the upper state, although interestingly not all of them are despite us seemingly having enough energy to put them there. This reflects the statistical nature of the distribution and is most easily thought of in terms of the classical translational energy described by the Maxwell distribution: the *average* energy may equal the energy gap but the atoms possess a range of energies, not all of which are suitable for providing the precise value for the quantum jump.

However, we have started to populate the upper level significantly and our classical instinct would be that as the temperature is raised further we would eventually give all particles this energy, and all would be in the upper state. But the Boltzmann distribution tells us that this is completely wrong, as can be seen by increasing T until $(\varepsilon/kT) = 10^{-4}$ say, when

$$\frac{n_1}{n_0} = e^{-0.0001} \approx e^0 = 1 \qquad (1.17)$$

That is, no matter how high we raise the temperature the most we can accomplish in this two-level singly-degenerate system is to equalise the populations of the two states, with $n_1 = n_0$. To an extent this reflects the fact that once kT exceeds ε an individual atom, for example, cannot accept energy since, as we have stressed above, it can only possess 0 or ε. The full variation of the number of particles in the upper state as the temperature is changed is shown in Figure 1.9(i). The population of the upper level increases exponentially from zero at 0 K but tends to the asymptotic value of $N/2$ at high temperature.

The energy of this system can now be calculated very simply since at any temperature n_0 particles have zero energy and n_1, ε:

$$E = n_0 \times 0 + n_1 \times \varepsilon = n_1\varepsilon \qquad (1.18)$$
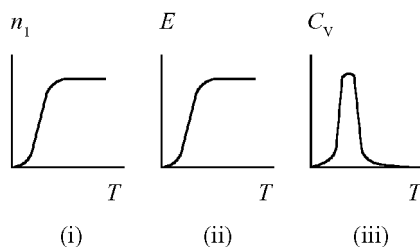
Figure 1.9 (i) *In a two-level system all the population is in the lower level at absolute zero but the number in the upper level (*n_1*) grows as the temperature is increased. It does not grow indefinitely, however, but reaches an asymptotic value at high temperature. If the levels are singly-degenerate, half of the total number of molecules is then in each level.* (ii) *The total energy of the system is the product of the population of the upper level times its energy (see text) and so it varies with temperature exactly as does* n_1*. The energy also reaches an asymptotic value at high temperature.* (iii) *Variation of* C_V*with temperature is given by the differential with respect to temperature of the energy curve,* (ii) *It starts from zero, goes through a maximum at the point of inflexion of the energy curve, and returns to zero at high temperature.*

This is a simple multiple of n_1 so that the variation of energy with temperature has exactly the same form as the variation of n_1 [Figure 1.9(ii)]. This is astonishing. It shows that as the temperature is increased E does not increase continually but again tends to an asymptote. To check this we must again turn to a calculation and measurement of C_V, which is obtained over the temperature range simply by differentiating Figure 1.9(ii). [$C_V = (\partial E/\partial T)_V$]. This is shown in Figure 1.9(iii). It predicts, what would be very strange in classical physics, that the heat capacity increases through a maximum and then falls to zero as the temperature is increased, and is what is observed experimentally.

This precise behaviour is unique to the two-level system. But the arguments we have used are not. Thus the Boltzmann distribution in any system, in which any particle may exist in any one of a number of discrete energy levels, always contains exponential terms in which quantised energies are compared with kT, and it is the values of these exponentials that largely determine level populations and all the physical properties of the sample. That is, they all depend upon the ratio (ε/kT). This simple realisation gives probably the most important insight into physical chemistry.

An example is seen if we extend the argument used above to calculate the energy of the two-level system to one with many levels. We realise that the particles are distributed amongst the levels each of which has its own characteristic quantised energy, ε_i, and we must sum the energies of them all. It follows that

$$E = \sum_i n_i \varepsilon_i \qquad (1.19)$$

This seemingly obvious statement has astounding implications when we realise what we have done. It says that if we know the values of the quantised energies, which we can determine from spectroscopy or calculate using quantum mechanics, then we can calculate a thermodynamic property. It establishes a direct relationship between the properties of individual atoms and molecules and the thermodynamic properties of samples made up of large numbers of them, and it is one of the fundamental equations of statistical thermodynamics. We shall return to it later.

1.7.3 Two-level Systems with Degeneracies Greater than Unity; Halogen Atoms

At room temperature the electrons in atoms are found exclusively in their lowest orbitals. This is because the higher orbitals are greatly separated in energy from them so that $(\varepsilon/kT) \gg 1$. This is true of the halogens, but with these the lowest level is split into two by spin–orbit coupling, which is smallest in fluorine and largest in iodine (Figure 1.10). Such coupling results because motion of the electrically charged electron around the nucleus in a p-orbital causes a magnetic field there that is experienced by the electron itself. However, the electron possesses spin angular momentum that causes it to have a quite separate magnetic moment. As with the proton in an external magnetic field the quantised electron magnetic moment can adopt just two orientations inside the field due to orbital motion, and two energy levels result. Experiment shows that the energy separation between them is very low compared with the energies separating the orbitals so that the halogens behave as if they were two-level systems at normal temperatures.
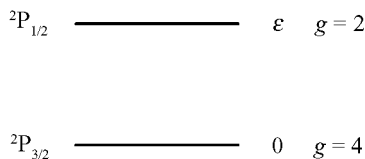
$$^2P_{1/2} \; \underline{\qquad} \qquad \varepsilon \quad g = 2$$

$$^2P_{3/2} \; \underline{\qquad} \qquad 0 \quad g = 4$$

Figure 1.10 *The lowest electronic energy level of the halogen atoms is split into two by spin–orbit coupling, the interaction between the magnetic moments due firstly to the orbital motion of the electron in its p-orbital and secondly due to its intrinsic spin. In fluorine the splitting in energy is of the order of kT at room temperature and both levels are populated. The next lowest electronic level is comparatively very high in energy (energy ≫ kT) and is completely unpopulated at room temperature. At this temperature the atoms behave as though they are two-level systems, but the two levels have different degeneracies.*

We take F as an example. Its electron configuration is $1s^2 2s^2 2p^5$ so that it has a single unpaired electron in a p-orbital. The states that result from spin–orbit coupling can be calculated simply using Term Symbols (Appendix 1.2) that show the ground state to split into $^2P_{1/2}$ and $^2P_{3/2}$ components. The subscript indicates the total angular momentum quantum number of the state, J, and according to Hund's rule the state with the highest J, $\frac{3}{2}$, lies lowest in energy when an electron shell is over half full. However, the Term Symbol has another crucial piece of information encoded in it since the degeneracy of a state is $(2J + 1)$, and we have seen that the degeneracy enters the Boltzmann distribution. For the upper state $g_1 = 2$ whilst for the lower one $g_0 = 4$ (Figure 1.10) so that

$$\frac{n_1}{n_0} = \frac{2}{4} e^{-\varepsilon/kT} \tag{1.20}$$

The exponential term changes with temperature exactly as before, tending to unity as $T \to \infty$. In consequence the asymptotic value of the ratio is no longer 1 but 0.5. That is, at high temperatures one-third of the atoms are in the upper state compared with the half obtained when the levels have equal degeneracies. Had the state with $J = \frac{3}{2}$ been the upper one then two-thirds of the atoms would have been in the upper state at the higher temperatures. Simply put, at high temperatures, a state of degeneracy g can hold g times more atoms than one of degeneracy one – the states behave as though they were buckets. Degeneracy has a significant effect on level populations.

Through the direct relationship between energy and heat capacity it is clear that the halogen atoms have C_V values that reflect their ability to accept electronic energy within these split ground state levels besides possessing translational energy.

It remains to put in some values to see how significant this is. Notably, the exponent always appears as a ratio so, provided that we express numerator and denominator in the same units, it does not matter what the units are. Spectroscopists measure ε using experimentally convenient reciprocal wavelength units, denoted $\bar{v}$ and usually quoted in cm^{-1} (1 cm $= 10^{-2}$ m). These are directly related to energy through the relations $E = hv$ and $c = v/\lambda$ or $c = v\bar{v}$, where v, λ and c are respectively the frequency, wavelength and velocity of the light. It follows that $E = hc/\bar{v}$. But rather than calculating this each time it is convenient to calculate kT/hc in cm^{-1} and to use the measurement units. (A discussion on units is provided in Appendix 2.1, Chapter 2). For F, $\varepsilon = 401$ cm^{-1}, whilst kT/hc at 298 K (room temperature) $= 207.2$ cm^{-1}, so that $\varepsilon/kT = 1.935$, and $e^{-\varepsilon/kT} = 0.144$. To work out the electronic contribution to the energy of 1

mole of F atoms at this temperature we first return to the Boltzmann distribution to obtain the number of atoms in the upper state:

$$\frac{n_1}{N_A} = \frac{g_1 e^{-\varepsilon/kT}}{g_0 e^{-0/kT} + g_1 e^{-\varepsilon/kT}} = \frac{2 \times 0.144}{4 + 2 \times 0.144} = 0.067 \qquad (1.21)$$

where, as usual, we have defined the lower state to have zero energy. The total electronic energy per mole at this temperature is $E = n_1 \varepsilon N_A = 0.067 \times 401 N_A$ cm^{-1} mol^{-1}, which is 328 J mol^{-1}. Thus the presence of the low-lying $^2P_{1/2}$ state increases the total energy of the system from the pure translation value of $12.47 \times 298 = 3716$ J mol^{-1} (recall $C_V = 12.47$ J mol^{-1} K^{-1} for translation) by roughly 9%. This increases rapidly with temperature.

The electronic heat capacity is given by $C_V = (dE/dT) = \varepsilon(dn_1/dT)$, where the latter is obtained by differentiating the previous equation.

1.7.4   A Molecular Example: NO Gas

NO is the only simple diatomic molecule that contains a single unpaired electron and it is in a π^* orbital, implying that it possesses one unit of orbital angular momentum about the bond axis, yielding a magnetic moment. Magnetic interaction with the electron spin magnetic moment once more results in spin–orbit coupling (Figure 1.11) and the ground state is split into two, giving $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states, with now the former the lower in energy. In diatomic molecules, as opposed to atoms, the degeneracies cannot be assessed from thesesymbols, but each is doubly degenerate ($g_0 = g_1 = 2$). The higher state lies 121 cm^{-1} above the lower so that at room temperature $\varepsilon/kT \approx 0.58$ and

$$\frac{n_1}{n_0} = \frac{2}{2} e^{-\varepsilon/kT} \approx 0.56 \qquad (1.22)$$

showing that over one-third of the molecules are in it at room temperature. As before, we could work out what this implies as a molar contribution to the total energy of the system but it is obviously appreciable, and so is the effect on the heat capacity. But, as with all light diatomic molecules, there is no contribution to the heat capacity at this temperature from vibrational motion, since the first excited vibrational level is too far removed in energy from the ground state to be occupied.

Clearly, it is simple to calculate the electronic energy and heat capacity of F and NO. But our calculations need not be restricted to these properties. A sample of NO at room temperature is found to be magnetic
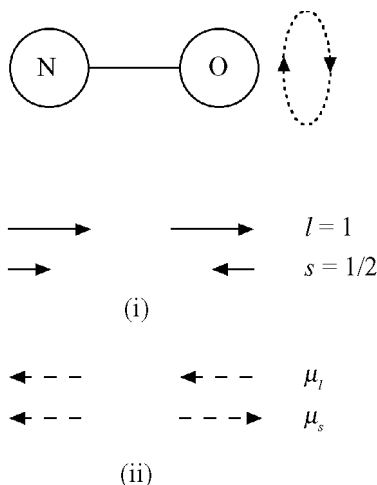
Figure 1.11 *In NO there is an unpaired electron in a π-orbital with orbital angular momentum (with quantum number l = 1) about the bond axis; the vector representing this is therefore drawn along this axis. (i) Relative to this the spin angular momentum vector of the electron (s = $\frac{1}{2}$) can lie either parallel to it, to give an overall momentum of $\frac{3}{2}$, or antiparallel to it $\frac{1}{2}$, leading to $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states. (ii) These motions of the negatively charged electron produce magnetic moments, also along the axis but in the opposite direction to the angular momentum vectors, and experiment shows that the magnetic moment due to spin motion is (almost) equal to that due to orbital motion. In the former state the moments add to make the state magnetic but in the latter the moments are opposed and the state is not magnetic. In the molecule, as opposed to the atom, each state is doubly degenerate (g = 2) and, with the next lowest molecular orbital well removed in energy from the lowest, NO behaves as a two-level system exactly as shown in Figure 1.9.*

(actually paramagnetic). At first sight this seems unsurprising in a molecule that contains an unpaired electron, since electrons are magnetic, but we must remember that in spin–orbit coupling we have discovered the influence of a second magnetic field within the molecule, due to orbital motion. We have therefore to consider the resultant magnetic field of the two rather than just that of electron spin. By quantum laws these can lie only parallel (the $^2\Pi_{3/2}$ state) or antiparallel (the $^2\Pi_{1/2}$ state) to each other along the molecular axis. In the former case the magnetic moments re-enforce each other, and in the latter they are opposed. It was discovered experimentally that the magnetic moment due to the spin motion is almost exactly equal (to 0.11%) to that due to orbital motion so that the two cancel in the $^2\Pi_{1/2}$ state, making it essentially non-magnetic. Since this is the lower energy state all the molecules would be in it at sufficiently low temperature and the sample would not be appreciably magnetic. That a room temperature sample is magnetic results from thermal population of the upper state.

A measure of the magnetism of a bulk sample is its susceptibility (χ, Greek chi) which is again straightforward to calculate. Calling the magnetic moment of a molecule in the $^2\Pi_{3/2}$ state μ, it is given by

$$\chi = n_{1/2} \times 0 + n_{3/2} \times \mu = n_{3/2}\mu \tag{1.23}$$

and $n_{3/2}$ per mole is obtained from the Boltzmann distribution as before (but remember $g_0 = g_1$ here). The temperature dependence of the susceptibility has exactly the same mathematical form as does the population of the upper state, and the energy of the system. It therefore increases from (near) zero at 0 K and rises to an asymptotic value. We see how powerful some rather straightforward ideas are in calculating the physical properties of collections of atoms and molecules.

APPENDIX 1.1   THE EQUIPARTITION INTEGRAL

From Equations (1.3) and (1.4),

$$\tfrac{1}{2}\,m\overline{u^2} = 2\pi m \left(\frac{m}{2\pi kT}\right)^{3/2} \int\limits_0^\infty e^{-mu^2/2kT} u^4 \, du \tag{1.24}$$

Since the standard integral

$$\int\limits_0^\infty e^{-ax^2} x^4 \, dx = \frac{3\pi^{1/2}}{8a^{5/2}} \tag{1.25}$$

we find that the terms in m cancel and

$$\tfrac{1}{2}m\overline{u^2} = \tfrac{3}{2}kT \tag{1.26}$$

This result obviously holds for any 'squared term' whose energy distribution is given by the Maxwell equation.

APPENDIX 1.2   TERM SYMBOLS

A Term Symbol provides a straightforward means for assessing what states of an atom exist as a result of spin–orbit coupling from knowledge of the electronic structure of the atom. In general an atom possesses many electrons and coupling occurs between their spin and orbital motions according to definite rules. For light atoms (those with low atomic numbers) *Russell–Saunders* coupling decrees that the spin and orbital angular momenta sum according to the rules:

$$S = \sum_i s_i \tag{1.27}$$

$$L = \sum_i l_i \tag{1.28}$$

where S is the vector sum of all the individual spin vectors of the electrons, s_i, and likewise for L; the quantum unit of angular momentum $(h/2\pi)$ is omitted by convention. The total angular momentum resulting from coupling between the magnetic moments due to these resultant momenta is then given by

$$J = L + S \tag{1.29}$$

A further convention is to write all these quantities in terms of the quantum numbers (scalars) rather than actual values of the angular momenta, despite having to remember that *vector* addition is involved. The result is expressed in the Term Symbol

$$^{2S+1}L_J \tag{1.30}$$

Orbital angular momentum quantum numbers of individual electrons are given letter symbols. Thus s, p, d and f refer to l values of 0, 1, 2 and 3 respectively. When the vector addition has taken place capital S, P, D and F symbols are used for the corresponding total L values.

   In filled electron shells individual s_i values cancel, as do the corresponding l_i ones, and we need consider only the unpaired electrons. In the F atom, with one unpaired electron in a 2p-orbital, $S = s_i = \frac{1}{2}$ and $L = l_i = 1$, which is a P state. By the general laws of quantum mechanics the two vectors can lie only parallel or antiparallel to each other, yielding just two possible values of J, $\frac{3}{2}$ and $\frac{1}{2}$. Their Term Symbols are $^2P_{3/2}$ and $^2P_{1/2}$ respectively, since $(2S + 1) = 2$. They are described as 'doublet P three halves' and 'doublet P half' states. Their energy separation depends on the spin–orbit coupling constant, which differs between different halogen atoms. From general quantum mechanical principles, the degeneracy of each state is given by $(2J + 1)$.

   With diatomic molecules a similar convention is used, except that the total angular momenta are summarised in Greek alphabet symbols, Σ (sigma), Π (pi), and Δ (delta) corresponding to S, P and D in atoms. The basic symbol becomes $^{2\Sigma+1}\Lambda$ where Σ is analogous to S and Λ (lambda) to L, and spin–orbit coupling may again occur between the two momenta. For NO with its single unpaired electron in a π^* orbital ($\Lambda = 1$, a Π state) the resultant states are, consequently, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. But these both have degeneracies of 2, not what we would expect for atoms. They are referred to as 'doublet Pi half' and 'doublet Pi three halves' states.

PROBLEMS

1.1 A linear molecule containing n atoms has 3 degrees of translational freedom, 2 degrees of rotational freedom and $(3n-5)$ degrees of vibrational freedom that contribute to its heat capacity. A non-linear one has 3, 3 and $(3n-6)$ degrees respectively.

Use the Equipartition Theorem to predict the molar internal energies and heat capacities of (i) O=C=O (linear) and (ii) H_2O (bent).

What would determine whether these values would be observed at 298 K?

1.2 In the nuclear magnetic resonance (NMR) experiment the degeneracy of the spin states of a spin-$\frac{1}{2}$ nucleus is removed by the application of an external magnetic field, B, measured in Tesla, T [see Figure 1.8(i)]. The energies of the resultant states are given by $m_I\mu B$ where $m_I = \pm\frac{1}{2}$ and μ is the magnetic moment; for the ^1H nucleus its value is 2.44×10^{-26} J T^{-1}. For 1 mole of H atoms in an external field of 14 T calculate

(i) the populations of the two spin states at 298 K. Why is it advantageous to perform the NMR experiment in the highest external field possible?

(ii) The contribution to the energy.

(iii) The magnetic susceptibility $[= (n_{\text{lower state}} - n_{\text{upper state}})\mu]$.

(iv) The transition frequency between the two states in the NMR experiment.

1.3 The electron is also a spin-$\frac{1}{2}$ particle, but its magnetic moment is -1.61×10^{-23} J T^{-1}. Electron spin resonance (ESR) experiments consist of exciting transitions between energy levels made non-degenerate by applying an external magnetic field. The negative sign makes the $m_S = +\frac{1}{2}$ state the lower in energy. If this experiment could also be performed in a 14 T field (it cannot at present for technical reasons) calculate the relative populations of the two energy levels. Assuming that the probability of causing a transition is the same in each case, what are the relative sensitivities of the ESR and NMR experiments?

1.4 The electronic ground state of F atoms is split by spin–orbit coupling as described in the text. The upper level is 401 cm^{-1} above the lower level. Calculate the population of the upper level of 1 mole of F atoms at (i) 298, (ii) 798 and (iii) 1298 K and the internal energy at these temperatures.

1.5 In Cl the spin–orbit splitting is 882.4 cm^{-1} and in Br it is 3685.0 cm^{-1}. The next lowest level in each case is at 71 958.4 and 63 436.5 cm^{-1}

respectively. Calculate the molar populations at 298 K of the upper of the two lowest states for both atoms in terms of N_A, and the electronic contribution to the energy per mole.

1.6   The lowest electronic energy level of O atoms is split into three by spin–orbit coupling. The Term Symbols of the states produced are $^3P_2$, $^3P_1$ and $^3P_0$, with energies of 0.00, 158.3 and 227.0 cm^{-1} respectively. What are the degeneracies of the three states? Use Equation (1.11) to calculate their relative populations at 298 K and then Equations (1.11) and (1.18) to calculate the electronic energy of 1 mole of O atoms. The next lowest level is at 15 867.9 cm^{-1}.

1.7   Alkali metals after Li have (core)np^1 electron configurations and therefore have ^2P ground states that are split by spin–orbit coupling. For Na, K, Rb and Cs the splittings are, respectively, 17.2, 57.7, 238 and 554 cm^{-1}. Assuming that in each case the next lowest level is so high in energy that all these metals behave as two-level systems, calculate the molar populations at 298 K of the levels in each in terms of N_A.

  For Cs, how close in energy would the next electronic level have to be for it to have a population approximately equal to 1% of that of the higher state? (Assume $g_{upper} = 1$ and that any change in the population of the $^2P_{3/2}$ is negligible; note that in these atoms the outermost shell is less than half-filled and so the $^2P_{1/2}$ state is the lower in energy.)