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## CHAPTER 1

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# Structure, energy, mechanism

### 1.1 Introduction

Physical chemistry is concerned with the structures of chemical compounds, the mechanisms by which these compounds react and the energy changes that accompany the reactions between the chemical species. Studies in these fundamental aspects of the subject are based largely upon experimental measurements, but theoretical and computer-simulation techniques provide powerful additional methods of investigation. Notwithstanding the subject has, for convenience here, been subdivided, the sections are inevitably linked, so that the order in which they are treated is simply a matter of preference.

All chapters are provided with sets of problems, for which detailed solutions are available on the Internet (see Preface), that have been designed to enhance the reader's appreciation of the subject matter. The reader is encouraged to attempt these problems, and the material described in Appendix 1 should be of assistance in this aspect of the study.

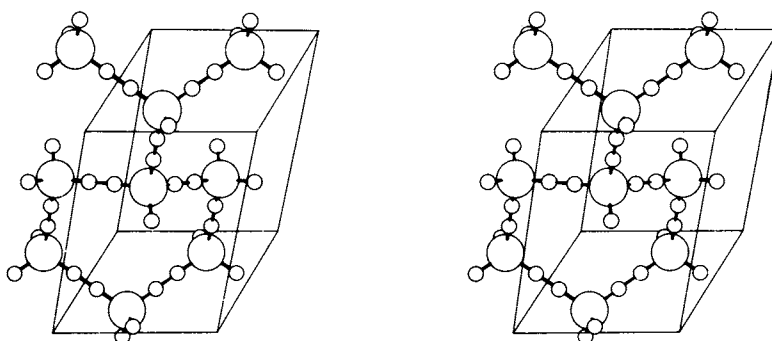
### 1.2 Structure

The term structure embraces a wide range of properties, among which we may include the stereochemistry of a molecule, the lengths of bonds between its atoms, the angles between pairs of bonds, the vibrations of atoms and groups of atoms, the distribution of electron density, the arrangement of molecules in the condensed state and the contact, or nonbonded, distances between species.

In the water molecule  $\text{H}_2\text{O}$ , for example, each hydrogen atom is linked to the oxygen atom by a bond that is mainly covalent, with O–H bond lengths of 0.096 nm and an H–O–H bond angle of  $104.4^\circ$ ; the distance between the two hydrogen atoms, the intramolecular proton separation, is 0.152 nm. These distances depend to a small extent on the method used to measure them. For example, X-ray diffraction provides distances between the electron density maxima of atoms, whereas neutron diffraction methods measure the distances between nuclei; generally, there will be a small but significant difference between the two results for one and the same bond length (see also Section 2.7.1).

Hydrogen and oxygen atoms have, formally, one and eight electrons respectively, but there is a shift of electronic charge when the atoms are combined, as in the water molecule. Theoretical calculations have shown that the charges on the hydrogen and oxygen atoms in a water molecule are approximately  $0.16e$  and  $-0.32e$  respectively, where  $e$  is the charge on an electron; the water molecule is said to be polar.

In the liquid state, the polarity of the water molecules leads to association between them. Relatively strong hydrogen bonds are set up: a hydrogen atom acts as an electrostatic link between two oxygen atoms, one in the same molecule as the hydrogen atom and the other in



**Figure 1.1** Stereoview of the unit cell and environs of the hydrogen-bonded structure of ice at 90 K. The circles represent, in decreasing order of size, oxygen and statistical half-hydrogen atoms. A tetrahedral disposition of bonds exists around any oxygen atom but, in any one molecule, only two of its four tetrahedral directions carry hydrogen atoms.

an adjacent molecule. These hydrogen bonds are continually breaking and reforming, and there exist constantly changing regions of water molecules in localized, approximately tetrahedral environments.

In ice at 90 K, there is nearly total hydrogen-bond formation between the water molecules, leading to a four-coordinate structure for ice. Figure 1.1 is a stereoview of the ice structure at 90 K; a discussion on stereoviewing is given in Appendix 2. In Figure 1.1, each small circle represents a statistically distributed half-hydrogen atom. At 313 K, the average number of hydrogen bonds is reduced to approximately one half of that at 90 K. The structure of ice is relatively open, or loosely packed, and a volume contraction occurs on melting. The non-bonded distance between adjacent oxygen atoms in ice is approximately 0.276 nm.

Hydrogen bonds are known to exist between hydrogen and several other atomic species, but are strongest in combination with fluorine, oxygen and nitrogen. The hydrogen bonds in water are responsible for many of the properties of this substance that appear to be anomalous when compared with related hydrides. The important chemical and biological functions of water depend upon the existence of its hydrogen bonds. Table 1.1 lists the boiling-point for a series of hydrides of periodic groups 15, 16 and 17. The values for the compounds in the first row are higher than would have been expected because, normally, the boiling-point temperature increases with an increase in the molar mass.

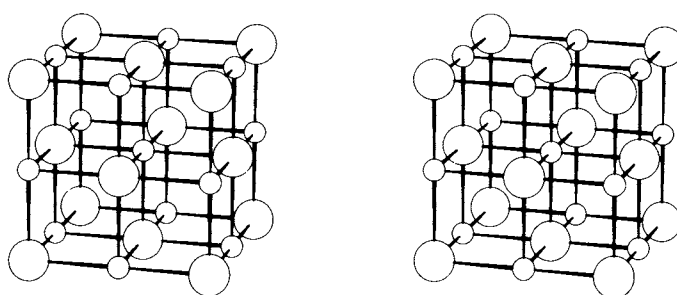
The existence of hydrogen-bonding in ammonia has been challenged on the grounds of spectroscopic and crystallographic evidence<sup>1</sup>. It is clear that, in the combination of ammonia with hydrogen fluoride, the lone pair of electrons on nitrogen bond to hydrogen; hence, a changing role for ammonia in combination with itself has been considered to be possible. From this premise, it would follow that liquid ammonia should behave differently from water and liquid hydrogen fluoride, but it is clear that more evidence is needed to resolve this question fully.

Many compounds do not exist as discrete molecules. Sodium chloride, for example, exists as ions in the solid state, linked together by Coulombic forces, but with no two ions preferentially associated with each other. The formula NaCl expresses the molar proportions of sodium to chlorine in the solid. If sodium chloride is heated, it melts at 1074 K to form a clear liquid containing sodium and chloride ions. The liquid boils at 1686 K, and the vapour consists of mainly covalent molecules of NaCl and Na<sub>2</sub>Cl<sub>2</sub>.

<sup>1</sup> D D Nelson *et al.* *Science* **238**, 1670 (1987).

**Table 1.1** Boiling-points/K for some hydrides

H <sub>3</sub> N	240	H <sub>2</sub> O	373	HF	254
H <sub>3</sub> P	186	H <sub>2</sub> S	213	HCl	188
H <sub>3</sub> As	218	H <sub>2</sub> Se	232	HBr	206
H <sub>3</sub> Sb	256	H <sub>2</sub> Te	271	HI	238



**Figure 1.2** Stereoview of the face-centred (F) cubic unit cell and environs of the sodium chloride structure. The circles represent, in decreasing order of size, Cl<sup>-</sup> and Na<sup>+</sup> ions. Each ion is coordinated by six ions of the opposite type, forming the apices of a regular octahedron about the given ion. There are four Na<sup>+</sup>Cl<sup>-</sup> pairs per unit cell.

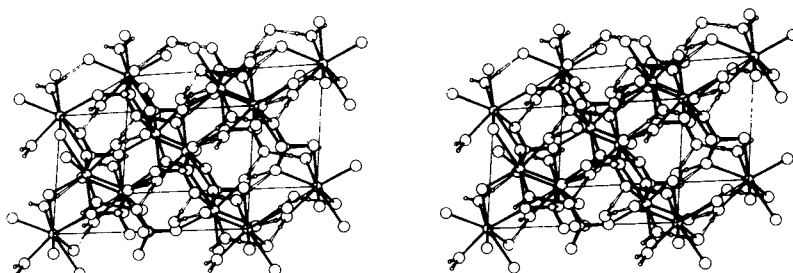
The structure of crystalline sodium chloride is illustrated by Figure 1.2. Pairs of sodium and chloride ions are associated with each point of a face-centred cubic unit cell (see Figure 3.13c later) of side 0.564 nm. These pairs Na<sup>+</sup>...Cl<sup>-</sup> are in identical vector orientations throughout the structure. The closest distances of ions are 0.282 nm for Na<sup>+</sup>...Cl<sup>-</sup> and 0.399 nm for Na<sup>+</sup>...Na<sup>+</sup> and Cl<sup>-</sup>...Cl<sup>-</sup>. The ideal macroscopic crystal of sodium chloride may be considered to be formed by packing unit cells together such that each face is common to, and shared by, two adjacent unit cells.

Calcium sulfate dihydrate (gypsum) CaSO<sub>4</sub>·2H<sub>2</sub>O has a quite different structure, Figure 1.3. The doubly charged sulfate anions are essentially covalently bonded entities, with S–O bond lengths of 0.16 nm, O–S–O angles of 109.5° and a tetrahedral geometry; they are linked to calcium cations by Coulombic forces. In addition, hydrogen-bonding occurs between the water molecules and the oxygen atoms of the sulfate ions; in fact, the hydrogen bonds maintain coherence of the structure in one direction.

### 1.3 Energy

Reactions take place with differing degrees of completeness. On the one hand, the reaction between hydrogen and oxygen to form liquid water is, for all practical purposes, complete and is accompanied by an enthalpy (heat content) change of approximately  $-286 \text{ kJ mol}^{-1}$ ; the negative sign implies that heat is *liberated* in the *exothermic* combination reaction. The energy of the hydrogen bonds in water accounts for 6 to 7% of this total enthalpy change. On the other hand, the dissolution of silver iodide in water at 298 K is negligible; its solubility at 298 K is  $1.02 \times 10^{-8} \text{ mol dm}^{-3}$ .

Between these extreme examples, all other stages of completion may be encountered with reacting systems. As an example, we consider the synthesis of ammonia by the Haber process,



**Figure 1.3** Stereoview of the unit cell and environs of the structure of calcium sulfate dihydrate. The circles represent, in decreasing order of size, O, Ca, S and H. The hydrogen bonds, shown in double lines (a hand-lens may help), are responsible for cohesion of the structure along the right-left direction in the illustration.

in which nitrogen and hydrogen at approximately 450°C and 200 atm are combined over a catalyst of  $\alpha$ -iron, in the presence of small amounts of oxides of iron, silicon and magnesium; the traces of oxides promote the reaction by increasing the active surface area of the catalyst.

The reaction is exothermic for the production of ammonia:



The  $\rightleftharpoons$  sign indicates that an equilibrium is attained between the components of the reaction at any given temperature and pressure. Tables 1.2 and 1.3 list some experimental results for this equilibrium. The equilibrium constant  $K_p$ , which is a measure of the completeness of a reaction, is given here by

$$K_p = \frac{p_{\text{NH}_3}}{p_{\text{N}_2}^{1/2} p_{\text{H}_2}^{3/2}} \quad (1.2)$$

where  $p$  represents partial pressure; evidently,  $K_p$  depends only on the temperature and decreases with an increase in this variable for the formation of ammonia by (1.1).

The percentage of ammonia at equilibrium increases with an increase in pressure, but decreases with an increase in temperature. These conclusions are in accord with the Le Chatelier–Braun principle, which states that *a system at equilibrium, when subjected to a perturbation, responds so as to tend to annul the effect of the perturbation.*

The production of ammonia, the forwards reaction in (1.1), is accompanied by a decrease in the *free energy*  $\Delta G$  of the system, given by

$$\Delta G = \Delta H - T \Delta S \quad (1.3)$$

A negative value of  $\Delta G$  for (1.1) is taken to indicate that the formation of ammonia is energetically feasible. The terms on the right-hand side of (1.3) represent respectively the change in enthalpy  $\Delta H$  and the change in entropy  $\Delta S$ , at the temperature  $T$ ;  $\Delta G$  is a sort of compromise parameter between  $\Delta H$  and  $\Delta S$ , which often act in opposition to each other.

At the temperatures considered in Tables 1.2 and 1.3  $\Delta G$  is actually positive. It would appear also that, at 298 K, the percentage of ammonia would be appreciably greater than that at, say, 700 K. This view is supported by the equilibrium equation<sup>2</sup>

$$\Delta G_m^{-0-} = -\mathcal{R}T \ln K_p \quad (1.4)$$

where  $\mathcal{R}$  is the gas constant.

<sup>2</sup> The superscript  $-0-$  refers to *standard* conditions (see Section 4.5); ‘ln’ stands for *logarithmus naturalis* (logarithm to the base e).

**Table 1.2** Nitrogen–hydrogen–ammonia equilibrium: percentage of ammonia at equilibrium as a function of temperature and pressure

<i>p</i> /atm	10	50	100
<i>T</i> /K			
623	10.4	25.1	37.1
673	3.85	15.1	24.9
723	2.04	9.17	16.4
773	1.20	5.58	10.4

**Table 1.3** Nitrogen–hydrogen–ammonia equilibrium: equilibrium constant  $K_p$  as a function of temperature<sup>3</sup>

<i>p</i> /atm	10	50	100
<i>T</i> /K			
623	0.0266	0.0278	0.0288
673	0.0129	0.0130	0.0137
723	0.00659	0.00690	0.00725
773	0.00381	0.00387	0.00402

Using Table 1.3, the molar free energy change  $\Delta G_m$  at 723 K is 30.2 kJ mol<sup>-1</sup>; at 298 K,  $\Delta G_m^{-0}$  is -16.5 kJ mol<sup>-1</sup>, and the corresponding equilibrium constant is 780. However, the rate of reaction at 298 K is extremely slow and optimum working conditions have to be chosen. We see how considerations of kinetics are now introduced. Notwithstanding the energetics at 298 K are favourable, the reactants must acquire a certain amount of energy, the activation energy, before reaction will take place at a measurable rate. Although a reaction at 298 K may be thermodynamically feasible, it need not take place immediately the reactants are mixed. We shall consider this reaction again in the chapter on thermodynamics.

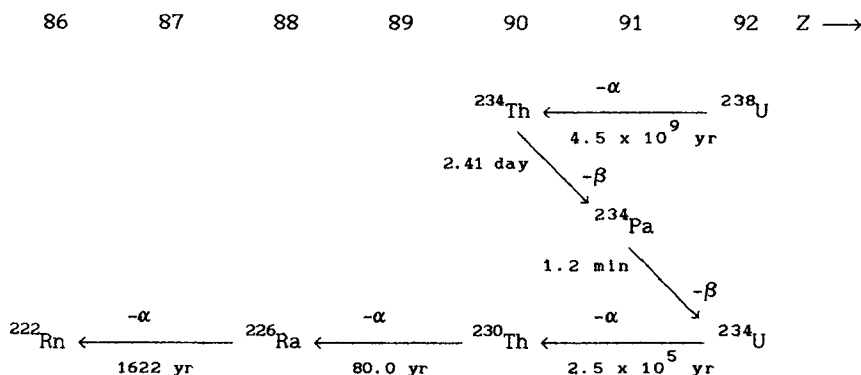
### 1.4 Mechanism

The mechanisms of chemical reactions include considerations of rate, molecularity and reaction pathway, and are usually derived from a study of the kinetics of reactions. For example, the formation of methoxyethane from iodomethane and sodium ethanoate in alcoholic solution occurs as a result of collisions between reactant molecules:



The rate of this reaction depends first upon how often the reactants meet each other, which events are proportional to their concentrations, and whether or no they collide with suffi-

<sup>3</sup> The small drift in  $K_p$  with pressure occurs because the partial pressure has been used in (1.2) rather than the fugacity (see Section 4.9.3).



**Figure 1.4** Radioactive decay in the  $^{238}\text{U}$  series between atomic numbers  $Z$  86 and 92:  $-\alpha$  and  $-\beta$  indicate emission of the corresponding radiations; the half-lives of the species are also given.

cient energy to drive the process forwards. Reaction (1.5) is bimolecular, that is, there are two molecular species involved in the process. It is also of second-order kinetics, because the rate is proportional to the concentrations of both reactants raised to the power of unity.

The decay of the nuclei of elements of atomic number greater than 83 (bismuth) is spontaneous and energy is emitted as  $\alpha$  or  $\beta$  radiation, Figure 1.4. The rate of radioactive decay depends only on the concentration of the radioactive species present; it is a first-order reaction.

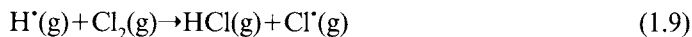
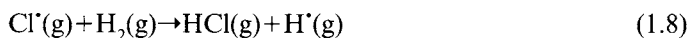
The apparently straightforward reaction between hydrogen and chlorine



is very slow unless activated by radiation of sufficient energy:



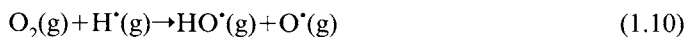
Here,  $\text{Cl}^*$  is a chlorine free radical, that is, a species having an unpaired electron;  $h\nu$  represents a photon, a packet of radiant energy, where  $h$  is the Planck constant and  $\nu$  is the frequency of the radiation, in this case in the ultraviolet (UV) region of the energy spectrum (Figure 1.5). A chain mechanism is set up, in which more free radicals are generated. If uncontrolled, the reaction will proceed at an explosive rate:



Reactions (1.5) and (1.6) differ in the way in which they acquire the energy necessary to initiate reaction: (1.5) by warming in alcoholic solution, (1.6) by UV irradiation.

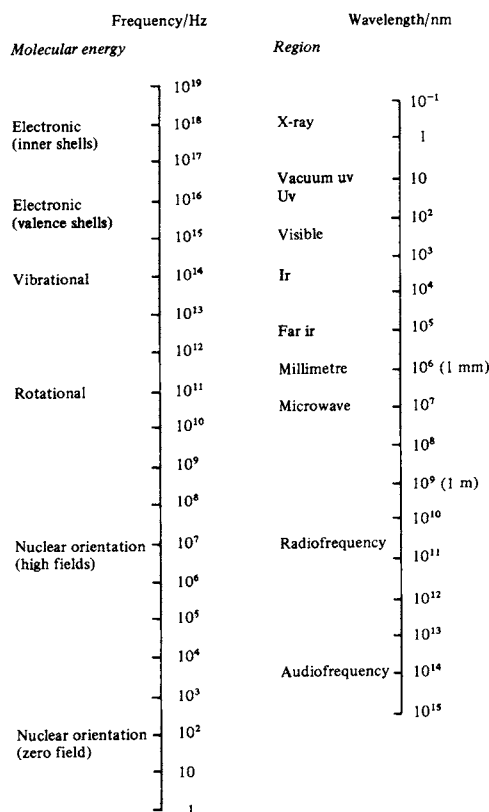
The bond dissociation enthalpies (or energies, if at 0 K) of hydrogen and chlorine molecules are approximately  $436 \text{ kJ mol}^{-1}$  and  $243 \text{ kJ mol}^{-1}$  respectively. It follows that (1.7) will be initiated if the system is supplied with energy somewhat greater than  $243 \text{ kJ mol}^{-1}$ , or  $4.04 \times 10^{-19} \text{ J}$  (2.5 eV) per molecule. This amount of energy corresponds to radiation of wavelength 492 nm; hence, bright visible light or UV radiation brings about a ready reaction.

Hydrogen and oxygen may be caused to combine at an explosive rate. Again, free radicals are involved and the process is complex. Branching reactions occur, in which the number of free radicals is increased greatly in the course of the reaction:



## Problems 1

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**Figure 1.5** Electromagnetic spectrum, with frequencies and wavelengths indicated for molecular energies throughout the spectrum.

Branching leads to a large increase in the rate of reaction, so that an explosion occurs when a mixture of hydrogen and oxygen is subjected to a high-energy radiation, such as an electric spark. Other reactions exist that terminate the chain process, such as



We discuss the kinetics of chemical reactions in more detail in Chapter 10.

Since kinetic studies involve the mechanisms of reactions, which may themselves be dependent upon structure, and because spontaneity of reaction depends upon energy changes, it is evident that the fundamental topics of structure, energy and mechanism are closely linked in the reactions of chemical species. In the ensuing chapters, we enlarge on these themes as we pursue our study of physical chemistry.

## Problems 1

1.1 In the molecule of  $\text{ClO}_2$ , the Cl–O bond distance is 149 pm and the distance between the two oxygen atoms is 254 pm. Calculate the O–Cl–O bond angle.

1.2 Assuming that no hydrogen-bonding existed in water, what would be its approximate boiling-point (refer to Table 1.1)?



- 1.3 In the sulfate ion, the excess charge associated nominally with each oxygen atom is  $-0.95e$ . What would be the corresponding nominal charge on the sulfur atom?
- 1.4 What is the second shortest sodium–chlorine distance in the sodium chloride structure; the cube side  $a$  equals 0.564 nm? Calculate the density of solid sodium chloride.
- 1.5 The energy needed to initiate a given chemical reaction is approximately  $400 \text{ kJ mol}^{-1}$ . What would be the wavelength of a suitable radiation source and in what region of the electromagnetic spectrum would the radiation occur?
- 1.6 The volume of gaseous helium, at 273 K and 1 atm, liberated by the radioactive disintegration of 1 g of radium during a period of 1 year is  $0.043 \text{ cm}^3$ . In the same time period, the number of  $\alpha$  particles emitted in the disintegration of the same amount of radium is  $116 \times 10^{16}$ . Assuming that each  $\alpha$  particle yields one atom of helium, calculate a value for the Avogadro constant  $N_A$ .



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 CHAPTER 2
 

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## Atoms, molecules and their structures

### 2.1 Introduction

Until the turn of the present century, it was believed that the behaviour of atoms was described by the classical mechanics of Newton, as was the case with macroscopic bodies. However, several experimental results seemed to be at variance with this assumption and in 1926 the new science of quantum mechanics was developed to explain the behaviour of microscopic particles. We shall consider in this chapter some aspects of quantum mechanics and see how classical mechanics is, in fact, a special case of this more general theory.

### 2.2 Classical mechanics

The behaviour of a classical particle can be described by two basic equations. In the first of them, the total energy  $E$  of a particle of mass  $m$  and speed  $v$ , at a position  $x$  and time  $t$  with respect to a given origin, is equal to the sum of its kinetic energy  $\frac{1}{2}mv^2$  and potential energy  $V(x)$ :

$$E = \frac{1}{2}mv^2 + V(x) \quad (2.1)$$

where  $v$  and  $x$  are functions of time  $t$ . We may also write

$$E = p^2/(2m) + V(x) \quad (2.2)$$

where  $p$  is the linear momentum. If we consider a constant potential energy, independent of  $x$ , we have

$$m \frac{dx}{dt} = [2m(E - V)]^{1/2} \quad (2.3)$$

whence by integration

$$x_t = x_0 + [2(E - V)/m]^{1/2}t \quad (2.4)$$

Using (2.2), we obtain

$$x_t = x_0 + p_0 t/m \quad (2.5)$$

and, since the total energy  $E$  is constant,

$$p_t = p_0 \quad (2.6)$$

Hence, for a given value of  $E$ , the values at any time both of  $x$  and of  $p$ , which constitute the trajectory of the particle, may be determined. The second basic equation depends on Newton's 2nd law (force = mass  $\times$  acceleration = rate of change of momentum):

$$F = m \frac{d^2x}{dt^2} = \frac{dp}{dt} \quad (2.7)$$

from which it may be shown that, for a given constant force, a particle may acquire any value for the energy  $E$ .

### 2.3 Conflict with experiment

The experimental results to which we referred at the start of this chapter conflicted both with the demand for continuous energy ranges and with the simultaneous knowledge of precise position and momentum that followed from the application of classical mechanics to atoms. We shall consider some of these results next, to see how they led towards the development of an improved atomic theory.

#### 2.3.1 Black-body radiation

An ideal *black body* is able to absorb or emit radiation of all frequencies (or energies) and is approximated well by a container with a pin-hole in one wall. If the container is heated, its temperature is indicated by its colour, because the radiation emitted from the hole is at the same temperature as the container, having been absorbed by and re-emitted from the interior of the walls many times; the emitted radiation is in thermal equilibrium with the walls of the black body. As the temperature of the radiator is increased, the frequency of the emitted radiation increases from the infrared end of the spectrum, through the visible range and into the ultraviolet region.

Figure 2.1 is a plot of an energy distribution  $E(\nu)$  as a function of the frequency  $\nu$ . The value  $\nu_{\max}$  at which  $E(\nu)$  is a maximum moves to higher frequencies as the temperature  $T$  is increased. Similar curves are obtained in terms of wavelength  $\lambda$ , but with  $\lambda_{\max}$  moving to lower wavelengths as the temperature is increased.

Experiments on black-body radiation by Stefan (1879) showed that the energy density  $\mathcal{E}$ , the total energy density per unit volume emitted over all wavelengths, followed the equation

$$\mathcal{E} = aT^4 \quad (2.8)$$

where the constant  $a$  was independent of the nature of the material of the body. In another set of experiments, Wien (1894) found

$$T\lambda_{\max} = b \quad (2.9)$$

where the experimentally determined value of  $b$  was  $2.9 \times 10^{-3}$  m K.

Rayleigh considered that black-body radiation was emitted by classical molecular oscillators, one for each frequency  $\nu$ ; the intensity of the radiation was taken to be proportional to the amplitude of oscillation. He determined the number density  $N(\nu)d\nu$  of oscillators with frequencies lying between  $\nu$  and  $\nu+d\nu$  inside a cubical enclosure of side  $c/\lambda$ , where  $c$  is the speed of light in a vacuum. The result, as amended later by Jeans, was

$$N(\nu)d\nu = (8\pi\nu^2/c^3)d\nu \quad (2.10)$$

We show in Appendix 3 that the mean energy of a classical oscillator at a temperature  $T$  is  $k_B T$ , where  $k_B$  is the Boltzmann constant. Hence, the required energy density, as given by the Rayleigh–Jeans equation, is

$$E(\nu)d\nu = N(\nu)k_B T d\nu = (8\pi\nu^2 k_B T/c^3)d\nu \quad (2.11)$$