

Fundamentals

Chemistry is the science of matter and the changes it can undergo. **Physical chemistry** is the branch of chemistry that establishes and develops the principles of the subject in terms of the underlying concepts of physics and the language of mathematics. It provides the basis for developing new spectroscopic techniques and their interpretation, for understanding the structures of molecules and the details of their electron distributions, and for relating the bulk properties of matter to their constituent atoms. Physical chemistry also provides a window on to the world of chemical reactions and allows us to understand in detail how they take place. In fact, the subject underpins the whole of chemistry, providing the principles in terms we use to understand structure and change and providing the basis of all techniques of investigation.

Throughout the text we shall draw on a number of concepts, most of which should already be familiar from introductory chemistry. This section reviews them. In almost every case the following chapters will provide a deeper discussion, but we are presuming that we can refer to these concepts at any stage of the presentation. Because physical chemistry lies at the interface between physics and chemistry, we also need to review some of the concepts from elementary physics that we need to draw on in the text.

F.1 Atoms

Key points (a) The nuclear model is the basis for discussion of atomic structure: negatively charged electrons occupy atomic orbitals, which are arranged in shells around a positively charged nucleus. (b) The periodic table highlights similarities in electronic configurations of atoms, which in turn lead to similarities in their physical and chemical properties. (c) Monatomic ions are electrically charged atoms and are characterized by their oxidation numbers.

Matter consists of atoms. The atom of an element is characterized by its **atomic number**, Z , which is the number of protons in its nucleus. The number of neutrons in a nucleus is variable to a small extent, and the **nucleon number** (which is also commonly called the *mass number*), A , is the total number of protons and neutrons, which are collectively called **nucleons**, in the nucleus. Atoms of the same atomic number but different nucleon number are the **isotopes** of the element.

According to the **nuclear model**, an atom of atomic number Z consists of a nucleus of charge $+Ze$ surrounded by Z electrons each of charge $-e$ (e is the fundamental charge: see inside the front cover for its value and the values of the other fundamental constants). These electrons occupy **atomic orbitals**, which are regions of space where they are most likely to be found, with no more than two electrons in any one orbital. The atomic orbitals are arranged in **shells** around the nucleus, each shell being characterized by the **principal quantum number**, $n = 1, 2, \dots$. A shell consists of n^2



F.1 Atoms

F.2 Molecules

F.3 Bulk matter

F.4 Energy

F.5 The relation between molecular and bulk properties

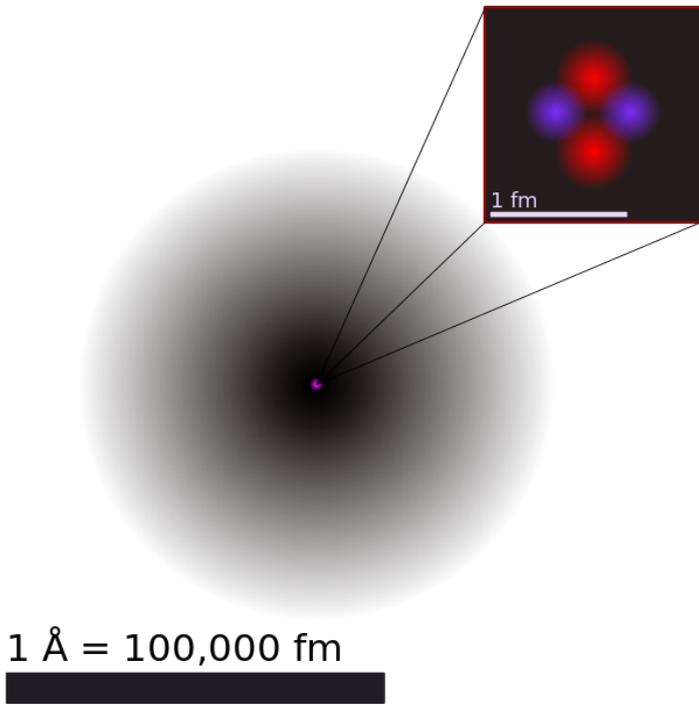
(a) The Boltzmann distribution

(b) Equipartition

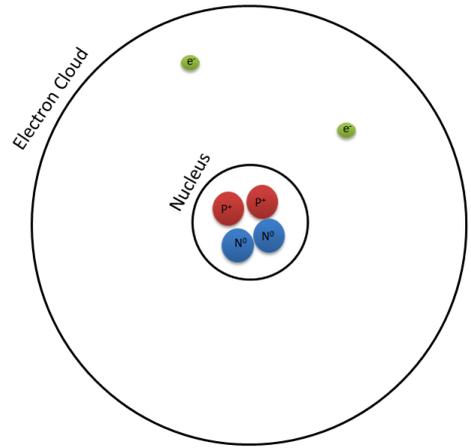
F.6 The electromagnetic field

F.7 Units

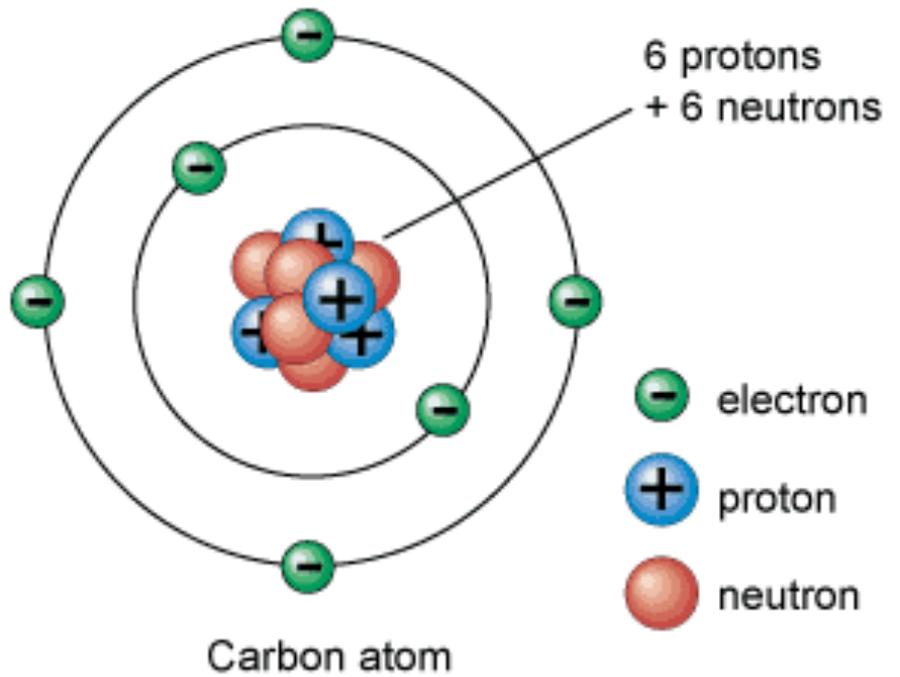
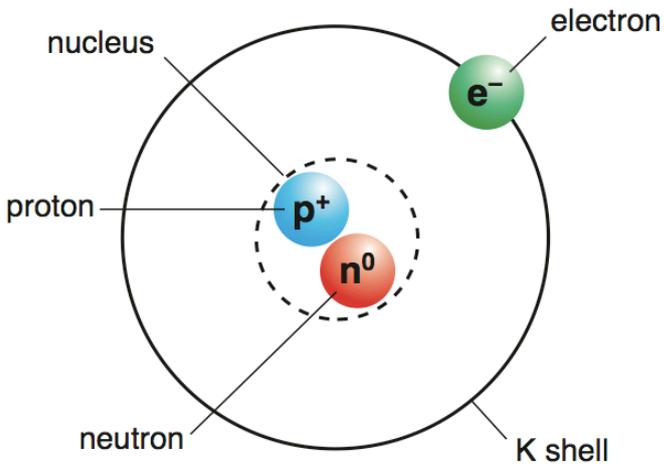
Exercises



Helium Atom Diagram



Proton- Red
Neutron- Blue
Electron- Green



individual orbitals, which are grouped together into n **subshells**; these subshells, and the orbitals they contain, are denoted s, p, d, and f. For all neutral atoms other than hydrogen, the subshells of a given shell have slightly different energies.

The sequential occupation of the orbitals in successive shells results in periodic similarities in the **electronic configurations**, the specification of the occupied orbitals, of atoms when they are arranged in order of their atomic number, which leads to the formulation of the **periodic table** (a version is shown inside the back cover). The vertical columns of the periodic table are called **groups** and (in the modern convention) numbered from 1 to 18. Successive rows of the periodic table are called **periods**, the number of the period being equal to the principal quantum number of the **valence shell**, the outermost shell of the atom. The periodic table is divided into s, p, d, and f **blocks**, according to the subshell that is last to be occupied in the formulation of the electronic configuration of the atom. The members of the d block (specifically the members of Groups 3–11 in the d block) are also known as the **transition metals**; those of the f block (which is not divided into numbered groups) are sometimes called the **inner transition metals**. The upper row of the f block (Period 6) consists of the **lanthanoids** (still commonly the ‘lanthanides’) and the lower row (Period 7) consists of the **actinoids** (still commonly the ‘actinides’). Some of the groups also have familiar names: Group 1 consists of the **alkali metals**, Group 2 (more specifically, calcium, strontium, and barium) of the **alkaline earth metals**, Group 17 of the **halogens**, and Group 18 of the **noble gases**. Broadly speaking, the elements towards the left of the periodic table are **metals** and those towards the right are **nonmetals**; the two classes of substance meet at a diagonal line running from boron to polonium, which constitute the **metalloids**, with properties intermediate between those of metals and nonmetals.

A monatomic **ion** is an electrically charged atom. When an atom gains one or more electrons it becomes a negatively charged **anion**; when it loses one or more electrons it becomes a positively charged **cation**. The charge number of an ion is called the **oxidation number** of the element in that state (thus, the oxidation number of magnesium in Mg^{2+} is +2 and that of oxygen in O^{2-} is -2). It is appropriate, but not always done, to distinguish between the oxidation number and the **oxidation state**, the latter being the physical state of the atom with a specified oxidation number. Thus, the oxidation number of magnesium is +2 when it is present as Mg^{2+} , and it is present *in* the oxidation state Mg^{2+} . The elements form ions that are characteristic of their location in the periodic table: metallic elements typically form cations by losing the electrons of their outermost shell and acquiring the electronic configuration of the preceding noble gas. Nonmetals typically form anions by gaining electrons and attaining the electronic configuration of the following noble gas.

F.2 Molecules

Key points (a) **Covalent compounds** consist of discrete molecules in which atoms are linked by covalent bonds. (b) **Ionic compounds** consist of cations and anions in a crystalline array. (c) Lewis structures are useful models of the pattern of bonding in molecules. (d) The valence-shell electron pair repulsion theory (VSEPR theory) is used to predict the three-dimensional structures of molecules from their Lewis structures. (e) The electrons in polar covalent bonds are shared unevenly between the bonded nuclei.

A **chemical bond** is the link between atoms. Compounds that contain a metallic element typically, but far from universally, form **ionic compounds** that consist of cations and anions in a crystalline array. The ‘chemical bonds’ in an ionic compound

are due to the Coulombic interactions (Section F.4) between all the ions in the crystal, and it is inappropriate to refer to a bond between a specific pair of neighbouring ions. The smallest unit of an ionic compound is called a **formula unit**. Thus NaNO_3 , consisting of a Na^+ cation and a NO_3^- anion, is the formula unit of sodium nitrate. Compounds that do not contain a metallic element typically form **covalent compounds** consisting of discrete molecules. In this case, the bonds between the atoms of a molecule are **covalent**, meaning that they consist of shared pairs of electrons.

The pattern of bonds between neighbouring atoms is displayed by drawing a **Lewis structure**, in which bonds are shown as lines and **lone pairs** of electrons, pairs of valence electrons that are not used in bonding, are shown as dots. Lewis structures are constructed by allowing each atom to share electrons until it has acquired an **octet** of eight electrons (for hydrogen, a *duplet* of two electrons). A shared pair of electrons is a **single bond**, two shared pairs constitute a **double bond**, and three shared pairs constitute a **triple bond**. Atoms of elements of Period 3 and later can accommodate more than eight electrons in their valence shell and ‘expand their octet’ to become **hypervalent**, that is, form more bonds than the octet rule would allow (for example, SF_6), or form more bonds to a small number of atoms (for example, a Lewis structure of SO_4^{2-} with one or more double bonds). When more than one Lewis structure can be written for a given arrangement of atoms, it is supposed that **resonance**, a blending of the structures, may occur and distribute multiple-bond character over the molecule (for example, the two Kekulé structures of benzene). Examples of these aspects of Lewis structures are shown in Fig. F.1.

Except in the simplest cases, a Lewis structure does not express the three-dimensional structure of a molecule. The simplest approach to the prediction of molecular shape is **valence-shell electron pair repulsion theory** (VSEPR theory). In this approach, the regions of high electron density, as represented by bonds—whether single or multiple—and lone pairs, take up orientations around the central atom that maximize their separations. Then the position of the attached atoms (not the lone pairs) is noted and used to classify the shape of the molecule. Thus, four regions of electron density adopt a tetrahedral arrangement; if an atom is at each of these locations (as in CH_4), then the molecule is tetrahedral; if there is an atom at only three of these locations (as in NH_3), then the molecule is trigonal pyramidal; and so on. The names of the various shapes that are commonly found are shown in Fig. F.2. In a refinement of the theory, lone pairs are assumed to repel bonding pairs more strongly than bonding pairs repel each other. The shape a molecule then adopts, if it is not

A note on good practice Some chemists use the term ‘molecule’ to denote the smallest unit of a compound with the composition of the bulk material regardless of whether it is an ionic or covalent compound and thus speak of ‘a molecule of NaCl ’. We use the term ‘molecule’ to denote a discrete covalently bonded entity (as in H_2O); for an ionic compound we use ‘formula unit’.

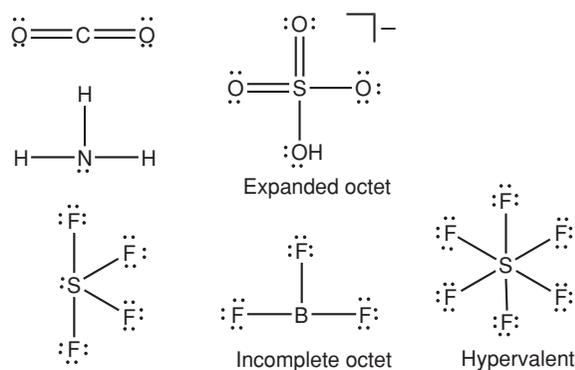


Fig. F.1 A collection of typical Lewis structures for simple molecules and ions. The structures show the bonding patterns and lone pairs and, except in simple cases, do not express the shape of the species.

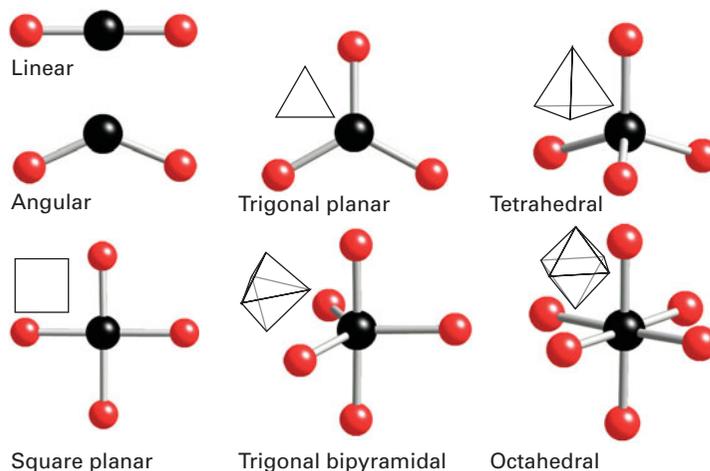


Fig. F.2 The names of the shapes of the geometrical figures used to describe symmetrical polyatomic molecules and ions.

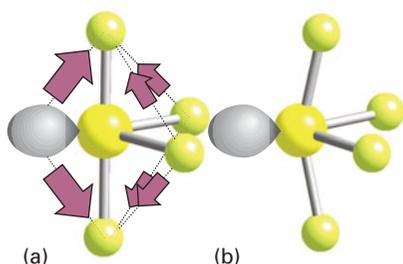


Fig. F.3 (a) The influences on the shape of the SF_4 molecule according to the VSEPR model. (b) As a result the molecule adopts a bent see-saw shape.

determined fully by symmetry, is such as to minimize repulsions from lone pairs. Thus, in SF_4 the lone pair adopts an equatorial position and the two axial S–F bonds bend away from it slightly, to give a bent see-saw shaped molecule (Fig. F.3).

Covalent bonds may be **polar**, or correspond to an unequal sharing of the electron pair, with the result that one atom has a partial positive charge (denoted $\delta+$) and the other a partial negative charge ($\delta-$). The ability of an atom to attract electrons to itself when part of a molecule is measured by the **electronegativity**, $\chi(\text{chi})$, of the element. The juxtaposition of equal and opposite partial charges constitutes an **electric dipole**. If those charges are $+Q$ and $-Q$ and they are separated by a distance d , the magnitude of the **electric dipole moment** is $\mu = Qd$. Whether or not a molecule as a whole is polar depends on the arrangement of its bonds, for in highly symmetrical molecules there may be no net dipole. Thus, although the linear CO_2 molecule (which is structurally OCO) has polar CO bonds, their effects cancel and the molecule as a whole is nonpolar.

F.3 Bulk matter

Key points (a) The physical states of bulk matter are solid, liquid, or gas. (b) The state of a sample of bulk matter is defined by specifying its properties, such as mass, volume, amount, pressure, and temperature. (c) The perfect gas law is a relation between the pressure, volume, amount, and temperature of an idealized gas.

Bulk matter consists of large numbers of atoms, molecules, or ions. Its physical state may be solid, liquid, or gas:

A **solid** is a form of matter that adopts and maintains a shape that is independent of the container it occupies.

A **liquid** is a form of matter that adopts the shape of the part of the container it occupies (in a gravitational field, the lower part) and is separated from the unoccupied part of the container by a definite surface.

A **gas** is a form of matter that immediately fills any container it occupies.

A liquid and a solid are examples of a **condensed state** of matter. A liquid and a gas are examples of a **fluid** form of matter: they flow in response to forces (such as gravity) that are applied.

The state of a bulk sample of matter is defined by specifying the values of various properties. Among them are:

The **mass**, m , a measure of the quantity of matter present (unit: kilogram, kg).

The **volume**, V , a measure of the quantity of space the sample occupies (unit: cubic metre, m^3).

The **amount of substance**, n , a measure of the number of specified entities (atoms, molecules, or formula units) present (unit: mole, mol).

An **extensive property** of bulk matter is a property that depends on the amount of substance present in the sample; an **intensive property** is a property that is independent of the amount of substance. The volume is extensive; the mass density, ρ (rho), the mass of a sample divided by its volume, $\rho = m/V$, is intensive.

The amount of substance, n (colloquially, ‘the number of moles’), is a measure of the number of specified entities present in the sample. ‘Amount of substance’ is the official name of the quantity; it is commonly simplified to ‘chemical amount’ or simply ‘amount’. The unit 1 mol is defined as the number of carbon atoms in exactly 12 g of carbon-12. The number of entities per mole is called **Avogadro’s constant**, N_A ; the currently accepted value is $6.022 \times 10^{23} \text{ mol}^{-1}$ (note that N_A is a constant with units, not a pure number). The **molar mass of a substance**, M (units: formally kilograms per mole but commonly grams per mole, g mol^{-1}) is the mass per mole of its atoms, its molecules, or its formula units. The amount of substance of specified entities in a sample can readily be calculated from its mass, by noting that

$$n = \frac{m}{M} \quad (\text{F.1})$$

A sample of matter may be subjected to a **pressure**, p (unit: pascal, Pa; $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$), which is defined as the force, F , it is subjected to, divided by the area, A , to which that force is applied. A sample of gas exerts a pressure on the walls of its container because the molecules of gas are in ceaseless, random motion and exert a force when they strike the walls. The frequency of the collisions is normally so great that the force, and therefore the pressure, is perceived as being steady. Although pascal is the SI unit of pressure (Section F.6), it is also common to express pressure in bar ($1 \text{ bar} = 10^5 \text{ Pa}$) or atmospheres ($1 \text{ atm} = 101\,325 \text{ Pa}$ exactly), both of which correspond to typical atmospheric pressure. We shall see that, because many physical properties depend on the pressure acting on a sample, it is appropriate to select a certain value of the pressure to report their values. The **standard pressure** for reporting physical quantities is currently defined as $p^\ominus = 1 \text{ bar}$ exactly. We shall see the role of the standard pressure starting in Chapter 2.

To specify the state of a sample fully it is also necessary to give its **temperature**, T . The temperature is formally a property that determines in which direction energy will flow as heat when two samples are placed in contact through thermally conducting walls: energy flows from the sample with the higher temperature to the sample with the lower temperature. The symbol T is used to denote the **thermodynamic temperature**, which is an absolute scale with $T = 0$ as the lowest point. Temperatures above $T = 0$ are then most commonly expressed by using the **Kelvin scale**, in which the gradations of temperature are called **kelvin** (K). The Kelvin scale is defined by setting the triple point of water (the temperature at which ice, liquid water, and water vapour are in mutual equilibrium) at exactly 273.16 K. The freezing point of water (the melting point of ice) at 1 atm is then found experimentally to lie 0.01 K below the triple point, so the freezing point of water is 273.15 K. The Kelvin scale is unsuitable for everyday

A note on good practice Be careful to distinguish atomic or molecular mass (the mass of a single atom or molecule; units kg) from molar mass (the mass per mole of atoms or molecules; units kg mol^{-1}). *Relative molecular masses* of atoms and molecules, $M_r = m/m_u$, where m is the mass of the atom or molecule and m_u is the atomic mass constant, are still widely called ‘atomic weights’ and ‘molecular weights’ even though they are dimensionless quantities and not weights (the gravitational force exerted on an object). Even IUPAC continues to use the terms ‘for historical reasons’.

A note on good practice Note that we write $T = 0$, not $T = 0 \text{ K}$. General statements in science should be expressed without reference to a specific set of units. Moreover, because T (unlike θ) is absolute, the lowest point is 0 regardless of the scale used to express higher temperatures (such as the Kelvin scale or the Rankine scale). Similarly, we write $m = 0$, not $m = 0 \text{ kg}$ and $l = 0$, not $l = 0 \text{ m}$.

measurements of temperature, and it is common to use the **Celsius scale**, which is defined in terms of the Kelvin scale as

$$\theta/^{\circ}\text{C} = T/\text{K} - 273.15 \quad \text{Definition of Celsius scale} \quad (\text{F.2})$$

Thus, the freezing point of water is 0°C and its boiling point (at 1 atm) is found to be 100°C (more precisely 99.974°C). Note that in this text T invariably denotes the thermodynamic (absolute) temperature and that temperatures on the Celsius scale are denoted θ (theta).

The properties that define the state of a system are not in general independent of one another. The most important example of a relation between them is provided by the idealized fluid known as a **perfect gas** (also, commonly, an ‘ideal gas’)

$$pV = nRT \quad \text{Perfect gas equation} \quad (\text{F.3})$$

Here R is the **gas constant**, a universal constant (in the sense of being independent of the chemical identity of the gas) with the value $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. Equation F.3 is central to the development of the description of gases in Chapter 1.

A note on good practice Although the term ‘ideal gas’ is almost universally used in place of ‘perfect gas’, there are reasons for preferring the latter term. In an ideal system (as will be explained in Chapter 5) the interactions between molecules in a mixture are all the same. In a perfect gas not only are the interactions all the same but they are in fact zero. Few, though, make this useful distinction.

F.4 Energy

Key points (a) Energy is the capacity to do work. (b) The total energy of a particle is the sum of its kinetic and potential energies. The kinetic energy of a particle is the energy it possesses as a result of its motion. The potential energy of a particle is the energy it possesses as a result of its position. (c) The Coulomb potential energy between two charges separated by a distance r varies as $1/r$.

Much of chemistry is concerned with transfers and transformations of energy, and it is appropriate to define this familiar quantity precisely: **energy** is the capacity to do work. In turn, work is defined as motion against an opposing force. The SI unit of energy is the joule (J), with

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

(see Section F.7).

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

$$E_{\text{k}} = \frac{1}{2}mv^2 \quad \text{Kinetic energy} \quad (\text{F.4})$$

The **potential energy**, E_{p} or more commonly V , of a body is the energy it possesses as a result of its position. No universal expression for the potential energy can be given because it depends on the type of force that the body experiences. For a particle of mass m at an altitude h close to the surface of the Earth, the gravitational potential energy is

$$V(h) = V(0) + mgh \quad \text{Gravitational potential energy} \quad (\text{F.5})$$

where g is the **acceleration of free fall** ($g = 9.81 \text{ m s}^{-2}$). The zero of potential energy is arbitrary, and in this case it is common to set $V(0) = 0$.

One of the most important forms of potential energy in chemistry is the **Coulomb potential energy**, the potential energy of the electrostatic interaction between two point electric charges. For a point charge Q_1 at a distance r in a vacuum from another point charge Q_2

$$V(r) = \frac{Q_1 Q_2}{4\pi\epsilon_0 r} \quad \text{Coulomb potential energy} \quad (\text{F.6})$$

It is conventional (as here) to set the potential energy equal to zero at infinite separation of charges. Then two opposite charges have a negative potential energy at finite separations, whereas two like charges have a positive potential energy. Charge is expressed in coulombs (C), often as a multiple of the fundamental charge, e . Thus, the charge of an electron is $-e$ and that of a proton is $+e$; the charge of an ion is ze , with z the **charge number** (positive for cations, negative for anions). The constant ϵ_0 (epsilon zero) is the **vacuum permittivity**, a fundamental constant with the value $8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$. In a medium other than a vacuum, the potential energy of interaction between two charges is reduced, and the vacuum permittivity is replaced by the **permittivity**, ϵ , of the medium. The permittivity is commonly expressed as a multiple of the vacuum permittivity

$$\epsilon = \epsilon_r \epsilon_0 \quad (\text{F.7})$$

with ϵ_r the dimensionless **relative permittivity** (formerly, the *dielectric constant*).

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

$$E = E_k + E_p \quad (\text{F.8})$$

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

F.5 The relation between molecular and bulk properties

Key points (a) The energy levels of confined particles are quantized. (b) The Boltzmann distribution is a formula for calculating the relative populations of states of various energies. (c) The equipartition theorem provides a way to calculate the energy of some systems.

The energy of a molecule, atom, or subatomic particle that is confined to a region of space is **quantized**, or restricted to certain discrete values. These permitted energies are called **energy levels**. The values of the permitted energies depend on the characteristics of the particle (for instance, its mass) and the extent of the region to which it is confined. The quantization of energy is most important—in the sense that the allowed energies are widest apart—for particles of small mass confined to small regions of space. Consequently, quantization is very important for electrons in atoms and molecules, but usually unimportant for macroscopic bodies. For particles in containers of macroscopic dimensions the separation of energy levels is so small that for all practical purposes the motion of the particles through space—their translational motion—is unquantized and can be varied virtually continuously. As we shall see in detail in Chapter 7, quantization becomes increasingly important as we change focus from rotational to vibrational and then to electronic motion. The separation of rotational energy levels (in small molecules, about 10^{-23} J or 0.01 zJ , corresponding to about 0.01 kJ mol^{-1}) is smaller than that of vibrational energy levels (about 10 kJ mol^{-1}), which itself is smaller than that of electronic energy levels (about 10^{-18} J or 1 aJ , corresponding to about 10^3 kJ mol^{-1}). Figure F.4 depicts these typical energy level separations.

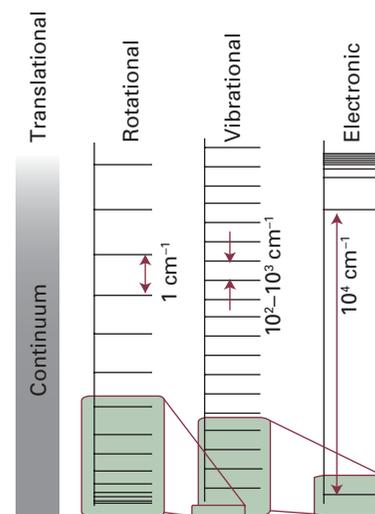


Fig. F.4 The energy level separations (expressed as wavenumbers) typical of four types of system.

A brief comment

The uncommon but useful prefixes **z** (for zepto) and **a** (for atto) are explained in Section F.7 on the use of units.

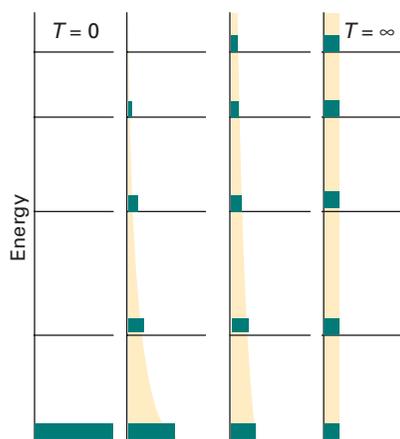


Fig. F.5 The Boltzmann distribution of populations for a system of five energy levels as the temperature is raised from zero to infinity.

(a) The Boltzmann distribution

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

The average number of molecules in a state is called the **population** of the state. Only the lowest energy state is occupied at $T = 0$. Raising the temperature excites some molecules into higher energy states, and more and more states become accessible as the temperature is raised further (Fig. F.5). The formula for calculating the relative populations of states of various energies is called the **Boltzmann distribution** and was derived by the Austrian scientist Ludwig Boltzmann towards the end of the nineteenth century. Although we shall derive and discuss this distribution in more detail in Chapter 15, at this point it is important to know that it gives the ratio of the numbers of particles in states with energies E_i and E_j as

$$\frac{N_i}{N_j} = e^{-(E_i - E_j)/kT} \quad \text{Boltzmann distribution} \quad (\text{F.9})$$

where k is **Boltzmann's constant**, a fundamental constant with the value $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$. This constant occurs throughout physical chemistry, often in a disguised (molar) form as the gas constant, for

$$R = N_A k \quad (\text{F.10})$$

where N_A is Avogadro's constant. We shall see in Chapter 15 that the Boltzmann distribution provides the crucial link for expressing the macroscopic properties of bulk matter in terms of the behaviour of its constituent atoms.

The important features of the Boltzmann distribution to bear in mind are:

- The higher the energy of a state, the lower its population.
- The higher the temperature, the more likely it is that a state of high energy is populated.
- More levels are significantly populated if they are close together in comparison with kT (like rotational and translational states), than if they are far apart (like vibrational and electronic states).

Figure F.6 summarizes the form of the Boltzmann distribution for some typical sets of energy levels. The peculiar shape of the population of rotational levels stems from the fact that eqn F.9 applies to *individual states*, and for molecular rotation the number of rotational states corresponding to a given energy increases with energy. Broadly speaking, the number of planes of rotation increases with energy. Therefore, although the population of each *state* decreases with energy, the population of the *levels* goes through a maximum.

One of the simplest examples of the relation between microscopic and bulk properties is provided by **kinetic molecular theory**, a model of a perfect gas. In this model, it is assumed that the molecules, imagined as particles of negligible size, are in ceaseless, random motion and do not interact except during their brief collisions. Different speeds correspond to different kinetic energies, so the Boltzmann formula can be used to predict the proportions of molecules having a specific speed at a particular temperature. The expression giving the fraction of molecules that have a particular speed is

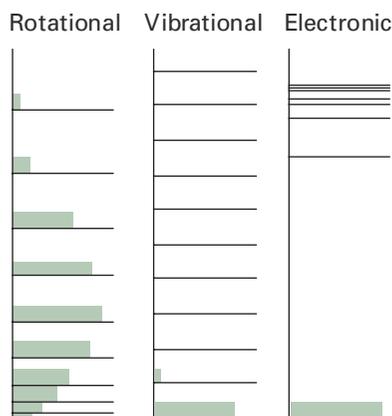


Fig. F.6 The Boltzmann distribution of populations for rotation, vibration, and electronic energy levels at room temperature.

called the **Maxwell distribution**, and has the features summarized in Fig. F.7. The Maxwell distribution, which is derived, specified, and discussed more fully in Chapter 20, can be used to show that the average speed, v_{mean} , of the molecules depends on the temperature and their molar mass as

$$v_{\text{mean}} \propto \left(\frac{T}{M}\right)^{1/2} \quad (\text{F.11})$$

That is, the average speed increases as the square-root of the temperature and decreases as the square-root of the molar mass. Thus, the average speed is high for light molecules at high temperatures. The distribution itself gives more information than the average value. For instance, the tail towards high speeds is longer at high temperatures than at low, which indicates that at high temperatures more molecules in a sample have speeds much higher than average.

(b) Equipartition

The Boltzmann distribution can be used to calculate the average energy associated with each mode of motion of a molecule (as we shall see in detail in Chapters 15 and 16). However, for certain modes of motion (which in practice means translation of any molecule and the rotation of all except the lightest molecules) there is a short cut, called the **equipartition theorem**. This theorem (which is derived from the Boltzmann distribution) states:

In a sample at a temperature T , all quadratic contributions to the total energy have the same mean value, namely $\frac{1}{2}kT$.

Equipartition theorem

A ‘quadratic contribution’ simply means a contribution that depends on the square of the position or the velocity (or momentum). For example, because the kinetic energy of a body of mass m free to undergo translation in three dimensions is $E_k = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$, there are three quadratic terms. The theorem implies that the average kinetic energy of motion parallel to the x -axis is the same as the average kinetic energy of motion parallel to the y -axis and to the z -axis. That is, in a normal sample (one at thermal equilibrium throughout), the total energy is equally ‘partitioned’ over all the available modes of motion. One mode of motion is not especially rich in energy at the expense of another. Because the average contribution of each mode is $\frac{1}{2}kT$, the average kinetic energy of a molecule free to move in three dimensions is $\frac{3}{2}kT$, as there are three quadratic contributions to the kinetic energy.

We shall often use the equipartition theorem to make quick assessments of molecular properties and to judge the outcome of the competition of the ordering effects of intermolecular interactions and the disordering effects of thermal motion.

F.6 The electromagnetic field

Key point Electromagnetic radiation is characterized by its direction of propagation, its wavelength, frequency, and wavenumber, and its state of polarization.

Light is a form of electromagnetic radiation. In classical physics, electromagnetic radiation is understood in terms of the **electromagnetic field**, an oscillating electric and magnetic disturbance that spreads as a harmonic wave through empty space, the vacuum. The wave travels at a constant speed called the *speed of light*, c , which is about $3 \times 10^8 \text{ m s}^{-1}$. As its name suggests, an electromagnetic field has two components, an **electric field** that acts on charged particles (whether stationary or moving) and a **magnetic field** that acts only on moving charged particles. The electromagnetic field,

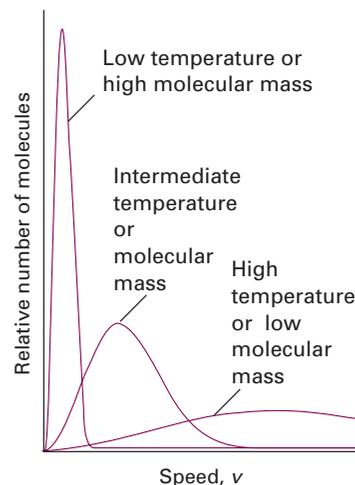


Fig. F.7 The distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increases with temperature and with decreasing molar mass, and simultaneously the distribution becomes broader.

interActivity (a) Plot different distributions by keeping the molar mass constant at 100 g mol^{-1} and varying the temperature of the sample between 200 K and 2000 K. (b) Use mathematical software or the *Living graph* applet from the text’s web site to evaluate numerically the fraction of molecules with speeds in the range 100 m s^{-1} to 200 m s^{-1} at 300 K and 1000 K. (c) Based on your observations, provide a molecular interpretation of temperature.

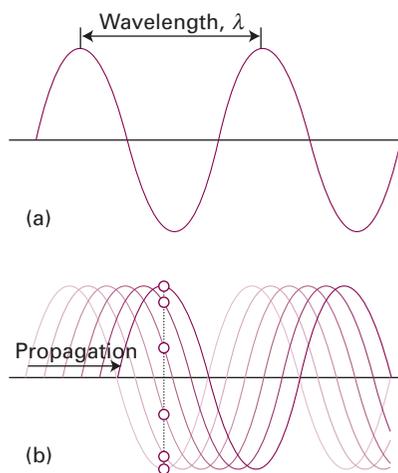


Fig. F.8 (a) The wavelength, λ , of a wave is the peak-to-peak distance. (b) The wave is shown travelling to the right at a speed c . At a given location, the instantaneous amplitude of the wave changes through a complete cycle (the six dots show half a cycle) as it passes a given point. The frequency, ν , is the number of cycles per second that occur at a given point. Wavelength and frequency are related by $\lambda\nu = c$.

A note on good practice You will hear people speaking of ‘a frequency of so many wavenumbers’. That is doubly wrong. First, wavenumber and frequency are two different physical observables. Second, wavenumber is a physical quantity, not a unit. The dimensions of wavenumber are $1/\text{length}$ and it is commonly reported in reciprocal centimetres, cm^{-1} .

like any periodic wave, is characterized by a **wavelength**, λ (lambda), the distance between the neighbouring peaks of the wave, and its **frequency**, ν (nu), the number of times in a given time interval at which its displacement at a fixed point returns to its original value divided by the length of the time interval, normally in seconds (Fig. F.8). The frequency is measured in *hertz*, where $1 \text{ Hz} = 1 \text{ s}^{-1}$. The wavelength and frequency of an electromagnetic wave are related by

$$\lambda\nu = c \quad (\text{F.12})$$

Therefore, the shorter the wavelength, the higher the frequency. The characteristics of a wave are also reported by giving the **wavenumber**, $\tilde{\nu}$ (nu tilde), of the radiation, where

$$\tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} \quad (\text{F.13})$$

A wavenumber can be interpreted as the number of complete wavelengths in a given length. Wavenumbers are normally reported in reciprocal centimetres (cm^{-1}), so a wavenumber of 5 cm^{-1} indicates that there are 5 complete wavelengths in 1 cm. A typical wavenumber of visible light is about $15\,000 \text{ cm}^{-1}$, corresponding to 15 000 complete wavelengths in each centimetre. The classification of the electromagnetic field according to its frequency and wavelength is summarized in Fig. F.9.

Electromagnetic radiation is **plane-polarized** if the electric and magnetic fields each oscillate in a single plane (Fig. F.10). The plane of polarization may be orientated in any direction around the direction of propagation with the electric and magnetic fields perpendicular to that direction (and perpendicular to each other). An alternative mode of polarization is **circular polarization**, in which the electric and magnetic fields rotate around the direction of propagation in either a clockwise or a counter-clockwise sense but remain perpendicular to it and each other.

According to classical electromagnetic theory, the intensity of electromagnetic radiation is proportional to the square of the amplitude of the wave. For example, the radiation detectors used in spectroscopy are based on the interaction between the electric field of the incident radiation and the detecting element, so light intensities are proportional to the square of the amplitude of the waves.

F.7 Units

Key points (a) The measurement of a physical property is expressed as the product of a numerical value and a unit. (b) In the International System of units (SI), the units are formed from seven base units, and all other physical quantities may be expressed as combinations of these physical quantities and reported in terms of derived units.

The measurement of a physical property is expressed as

$$\text{Physical property} = \text{numerical value} \times \text{unit}$$

For example, a length (l) may be reported as $l = 5.1 \text{ m}$, if it is found to be 5.1 times as great as a defined unit of length, namely, 1 metre (1 m). Units are treated as algebraic quantities, and may be multiplied and divided. Thus, the same length could be reported as $l/m = 5.1$. The symbols for physical properties are always italic (sloping; thus V for volume, not V), including Greek symbols (thus, μ for electric dipole moment, not μ), but available typefaces are not always so obliging.

In the **International System** of units (SI, from the French *Système International d’Unités*), the units are formed from seven **base units** listed in Table F.1. All other physical quantities may be expressed as combinations of these physical quantities and

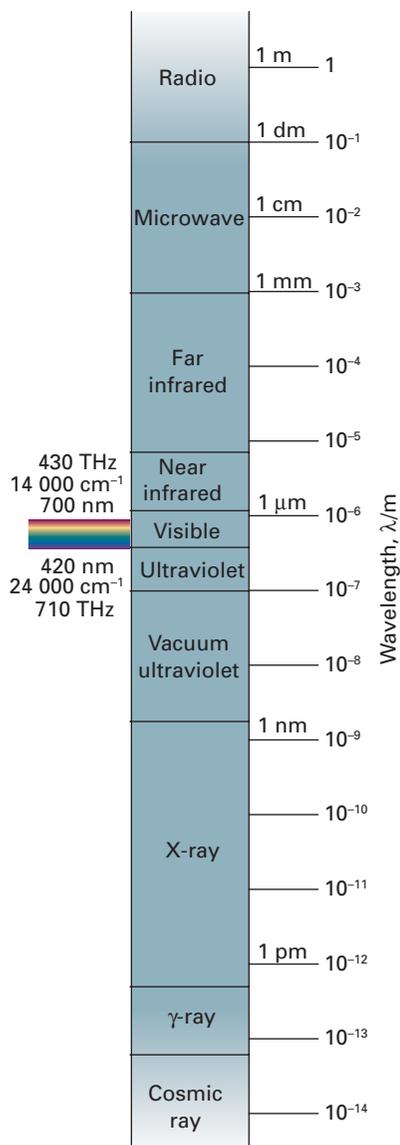


Fig. F.9 The regions of the electromagnetic spectrum. The boundaries are only approximate.

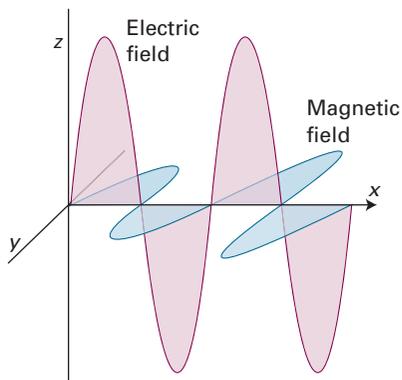


Fig. F.10 Electromagnetic radiation consists of a wave of electric and magnetic fields perpendicular to the direction of propagation (in this case the x -direction), and mutually perpendicular to each other. This illustration shows a plane-polarized wave, with the electric and magnetic fields oscillating in the xz - and xy -planes, respectively.

Table F.1 The SI base units

Physical quantity	Symbol for quantity	Base unit
Length	l	metre, m
Mass	m	kilogram, kg
Time	t	second, s
Electric current	I	ampere, A
Thermodynamic temperature	T	kelvin, K
Amount of substance	n	mole, mol
Luminous intensity	I_v	candela, cd

Table F.2 A selection of derived units

Physical quantity	Derived unit*	Name of derived unit
Force	1 kg m s ⁻²	newton, N
Pressure	1 kg m ⁻¹ s ⁻² 1 N m ⁻²	pascal, Pa
Energy	1 kg m ² s ⁻² 1 N m 1 Pa m ³	joule, J
Power	1 kg m ² s ⁻³ 1 J s ⁻¹	watt, W

* Equivalent definitions in terms of derived units are given following the definition in terms of base units.

Table F.3 Common SI prefixes

Prefix	y	z	a	f	p	n	μ	m	c	d
Name	yocto	zepto	atto	femto	pico	nano	micro	milli	centi	deci
Factor	10 ⁻²⁴	10 ⁻²¹	10 ⁻¹⁸	10 ⁻¹⁵	10 ⁻¹²	10 ⁻⁹	10 ⁻⁶	10 ⁻³	10 ⁻²	10 ⁻¹
Prefix	da	h	k	M	G	T	P	E	Z	Y
Name	deca	hecto	kilo	mega	giga	tera	peta	exa	zeta	yotta
Factor	10	10 ²	10 ³	10 ⁶	10 ⁹	10 ¹²	10 ¹⁵	10 ¹⁸	10 ²¹	10 ²⁴

reported in terms of **derived units**. Thus, volume is (length)³ and may be reported as a multiple of 1 metre cubed (1 m³), and density, which is mass/volume, may be reported as a multiple of 1 kilogram per metre cubed (1 kg m⁻³).

A number of derived units have special names and symbols. The names of units derived from names of people are lower case (as in torr, joule, pascal, and kelvin), but their symbols are upper case (as in Torr, J, Pa, and K). The most important for our purposes are listed in Table F.2.

In all cases (both for base and derived quantities), the units may be modified by a prefix that denotes a factor of a power of 10. The Greek prefixes of units are upright (as in μm, not μm). Among the most common prefixes are those listed in Table F.3. Examples of the use of these prefixes are

$$1 \text{ nm} = 10^{-9} \text{ m} \quad 1 \text{ ps} = 10^{-12} \text{ s} \quad 1 \text{ μmol} = 10^{-6} \text{ mol}$$

The kilogram (kg) is anomalous: although it is a base unit, it is interpreted as 10³ g, and prefixes are attached to the gram (as in 1 mg = 10⁻³ g). Powers of units apply to the prefix as well as the unit they modify

$$1 \text{ cm}^3 = 1 (\text{cm})^3 = 1 (10^{-2} \text{ m})^3 = 10^{-6} \text{ m}^3$$

Note that 1 cm³ does not mean 1 c(m³). When carrying out numerical calculations, it is usually safest to write out the numerical value of an observable as a power of 10.

There are a number of units that are in wide use but are not a part of the International System. Some are exactly equal to multiples of SI units. These include the *litre* (L), which is exactly 10³ cm³ (or 1 dm³) and the *atmosphere* (atm), which is exactly 101.325 kPa. Others rely on the values of fundamental constants, and hence are liable to change when the values of the fundamental constants are modified by more accurate

Table F.4 Some common units

Physical quantity	Name of unit	Symbol for unit	Value*
Time	minute	min	60 s
	hour	h	3600 s
	day	d	86 400 s
	year	a	31 556 952 s
Length	ångström	Å	10^{-10} m
Volume	litre	L, l	1 dm ³
Mass	tonne	t	10 ³ kg
Pressure	bar	bar	10 ⁵ Pa
	atmosphere	atm	101.325 kPa
Energy	electronvolt	eV	$1.602\ 176\ 53 \times 10^{-19}$ J
			96.485 31 kJ mol ⁻¹

* All values in the final column are exact, except for the definition of 1 eV, which depends on the measured value of e , and the year, which is not a constant and depends on a variety of astronomical assumptions.

or more precise measurements. Thus, the size of the energy unit *electronvolt* (eV), the energy acquired by an electron that is accelerated through a potential difference of exactly 1 V, depends on the value of the charge of the electron, and the present (2008) conversion factor is $1\text{ eV} = 1.602\ 176\ 53 \times 10^{-19}\text{ J}$. Table F.4 gives the conversion factors for a number of these convenient units.

Exercises

F.1 Atoms

- F1.1(a)** Summarize the nuclear model of the atom.
- F1.1(b)** Define the terms atomic number, nucleon number, mass number.
- F1.2(a)** Express the typical ground-state electron configuration of an atom of an element in (a) Group 2, (b) Group 7, (c) Group 15 of the periodic table.
- F1.2(b)** Express the typical ground-state electron configuration of an atom of an element in (a) Group 3, (b) Group 5, (c) Group 13 of the periodic table.
- F1.3(a)** Identify the oxidation numbers of the elements in (a) MgCl₂, (b) FeO, (c) Hg₂Cl₂.
- F1.3(b)** Identify the oxidation numbers of the elements in (a) CaH₂, (b) CaC₂, (c) LiN₃.
- F1.4(a)** Where in the periodic table are metals and nonmetals found?
- F1.4(b)** Where in the periodic table are transition metals, lanthanoids, and actinoids found?

F.2 Molecules

- F2.1(a)** Summarize what is meant by a single and multiple bond.
- F2.1(b)** Identify a molecule with (a) one, (b) two, (c) three lone pairs on the central atom.

- F2.2(a)** Draw the Lewis (electron dot) structures of (a) SO₃²⁻, (b) XeF₄, (c) P₄.
- F2.2(b)** Draw the Lewis (electron dot) structures of (a) O₃, (b) ClF₃⁺, (c) N₃⁻.
- F2.3(a)** Summarize the principal concepts of the VSEPR theory of molecular shape.
- F2.3(b)** Identify four hypervalent compounds.
- F2.4(a)** Use VSEPR theory to predict the structures of (a) PCl₃, (b) PCl₅, (c) XeF₂, (d) XeF₄.
- F2.4(b)** Use VSEPR theory to predict the structures of (a) H₂O₂, (b) FSO₃⁻, (c) KrF₂, (d) PCl₄⁺.
- F2.5(a)** Identify the polarities (by attaching partial charges δ^+ and δ^-) of the bonds (a) C–Cl, (b) P–H, (c) N–O.
- F2.5(b)** Identify the polarities (by attaching partial charges δ^+ and δ^-) of the bonds (a) C–H, (b) P–S, (c) N–Cl.
- F2.6(a)** State whether you expect the following molecules to be polar or nonpolar: (a) CO₂, (b) SO₂, (c) N₂O, (d) SF₄.
- F2.6(b)** State whether you expect the following molecules to be polar or nonpolar: (a) O₃, (b) XeF₂, (c) NO₂, (d) C₆H₁₄.
- F2.7(a)** Arrange the molecules in Exercise F2.6a by increasing dipole moment.
- F2.7(b)** Arrange the molecules in Exercise F2.6b by increasing dipole moment.

F.3 Bulk matter

F3.1(a) Compare and contrast the properties of the solid, liquid, and gas states of matter.

F3.1(b) Compare and contrast the properties of the condensed and gaseous states of matter.

F3.2(a) Classify the following properties as extensive or intensive: (a) mass, (b) mass density, (c) temperature, (d) number density.

F3.2(b) Classify the following properties as extensive or intensive: (a) pressure, (b) specific heat capacity, (c) weight, (d) molality.

F3.3(a) Calculate (a) the amount of C_2H_5OH (in moles) and (b) the number of molecules present in 25.0 g of ethanol.

F3.3(b) Calculate (a) the amount of $C_6H_{12}O_6$ (in moles) and (b) the number of molecules present in 5.0 g of glucose.

F3.4(a) Express a pressure of 1.45 atm in (a) pascal, (b) bar.

F3.4(b) Express a pressure of 222 atm in (a) pascal, (b) bar.

F3.5(a) Convert blood temperature, 37.0°C , to the Kelvin scale.

F3.5(b) Convert the boiling point of oxygen, 90.18 K, to the Celsius scale.

F3.6(a) Equation F.2 is a relation between the Kelvin and Celsius scales. Devise the corresponding equation relating the Fahrenheit and Celsius scales and use it to express the boiling point of ethanol (78.5°C) in degrees Fahrenheit.

F3.6(b) The Rankine scale is a version of the thermodynamic temperature scale in which the degrees ($^\circ\text{R}$) are the same size as degrees Fahrenheit. Derive an expression relating the Rankine and Kelvin scales and express the freezing point of water in degrees Rankine.

F3.7(a) A sample of hydrogen gas was found to have a pressure of 110 kPa when the temperature was 20.0°C . What is its pressure expected to be when the temperature is 7.0°C ?

F3.7(b) A sample of 325 mg of neon occupies 2.00 dm^3 at 20.0°C . Use the perfect gas law to calculate the pressure of the gas.

F.4 Energy

F4.1(a) Define energy and work.

F4.1(b) Distinguish between kinetic and potential energy.

F4.2(a) Consider a region of the atmosphere of volume 25 dm^3 that at 20°C contains about 1.0 mol of molecules. Take the average molar mass of the molecules as 29 g mol^{-1} and their average speed as about 400 m s^{-1} . Estimate the energy stored as molecular kinetic energy in this volume of air.

F4.2(b) Calculate the minimum energy that a bird of mass 25 g must expend in order to reach a height of 50 m.

F4.3(a) The potential energy of a charge Q_1 in the presence of another charge Q_2 can be expressed in terms of the *Coulomb potential*, ϕ (phi):

$$V = Q_1\phi \quad \phi = \frac{Q_2}{4\pi\epsilon_0 r}$$

The units of potential are joules per coulomb, J C^{-1} so, when ϕ is multiplied by a charge in coulombs, the result is in joules. The combination joules per coulomb occurs widely and is called a volt (V), with $1\text{ V} = 1\text{ J C}^{-1}$. Calculate the Coulomb potential due to the nuclei at a point in a LiH molecule located at 200 pm from the Li nucleus and 150 pm from the H nucleus.

F4.3(b) Plot the Coulomb potential due to the nuclei at a point in a Na^+Cl^- ion pair located on a line halfway between the nuclei (the internuclear

separation is 283 pm) as the point approaches from infinity and ends at the midpoint between the nuclei.

F.5 The relation between molecular and bulk properties

F5.1(a) What is meant by quantization of energy?

F5.1(b) In what circumstances are the effects of quantization most important for microscopic systems?

F5.2(a) The unit 1 electronvolt (1 eV) is defined as the energy acquired by an electron as it moves through a potential difference of 1 V. Suppose two states differ in energy by 1.0 eV. What is the ratio of their populations at (a) 300 K, (b) 3000 K?

F5.2(b) Suppose two states differ in energy by 1.0 eV, what can be said about their populations when $T = 0$ and when the temperature is infinite?

F5.3(a) What are the assumptions of the kinetic molecular theory?

F5.3(b) What are the main features of the Maxwell distribution of speeds?

F5.4(a) Suggest a reason why most molecules survive for long periods at room temperature.

F5.4(b) Suggest a reason why the rates of chemical reactions typically increase with increasing temperature.

F5.5(a) Calculate the relative mean speeds of N_2 molecules in air at 0°C and 40°C .

F5.5(b) Calculate the relative mean speeds of CO_2 molecules in air at 20°C and 30°C .

F5.6(a) Use the equipartition theorem to calculate the contribution of translational motion to the total energy of 5.0 g of argon at 25°C .

F5.6(b) Use the equipartition theorem to calculate the contribution of translational motion to the total energy of 10.0 g of helium at 30°C .

F5.7(a) Use the equipartition theorem to calculate the contribution to the total energy of a sample of 10.0 g of (a) carbon dioxide, (b) methane at 20°C ; take into account translation and rotation but not vibration.

F5.7(b) Use the equipartition theorem to calculate the contribution to the total internal energy of a sample of 10.0 g of lead at 20°C , taking into account the vibrations of the atoms.

F.6 The electromagnetic field

F6.1(a) Express a wavelength of 230 nm as a frequency.

F6.1(b) Express a wavelength of 720 nm as a frequency.

F6.2(a) Express a frequency of 560 THz as a wavenumber.

F6.2(b) Express a frequency of 160 MHz as a wavenumber.

F6.3(a) A radio station broadcasts at a frequency of 91.7 MHz. What is (a) the wavelength, (b) the wavenumber of the radiation?

F6.3(b) A spectroscopic technique uses microwave radiation of wavelength 3.0 cm. What is (a) the wavenumber, (b) the frequency of the radiation?

F.7 Units

F7.1(a) Express a volume of 1.45 cm^3 in cubic metres.

F7.1(b) Express a volume of 1.45 dm^3 in cubic centimetres.

F7.2(a) Express a mass density of 11.2 g cm^{-3} in kilograms per cubic metre.

F7.2(b) Express a mass density of 1.12 g dm^{-3} in kilograms per cubic metre.

F7.3(a) Express pascal per joule in base units.

F7.3(b) Express $(\text{joule})^2$ per $(\text{newton})^3$ in base units.

F7.4(a) The expression kT/hc sometimes appears in physical chemistry. Evaluate this expression at 298 K in reciprocal centimetres (cm^{-1}).

F7.4(b) The expression kT/e sometimes appears in physical chemistry. Evaluate this expression at 298 K in millielectronvolts (meV).

F7.5(a) Given that $R = 8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$, express R in decimetre cubed atmospheres per kelvin per mole.

F7.5(b) Given that $R = 8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$, express R in pascal centimetre cubed per kelvin per molecule.

F7.6(a) Convert $1 \text{ dm}^3 \text{ atm}$ into joules.

F7.6(b) Convert 1 J into litre-atmospheres.

F7.7(a) Determine the SI units of $e^2/\epsilon_0 r^2$. Express them in (a) base units, (b) units containing newtons.

F7.7(b) Determine the SI units of $\mu_B^2/\mu_0 r^3$, where μ_B is the Bohr magneton ($\mu_B = e\hbar/2m_e$) and μ_0 is the vacuum permeability (see inside front cover). Express them in (a) base units, (b) units containing joules.

General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.997 925 58*	10^8	m s^{-1}
Elementary charge	e	1.602 176	10^{-19}	C
Faraday's constant	$F = N_A e$	9.648 53	10^4	C mol^{-1}
Boltzmann's constant	k	1.380 65	10^{-23}	J K^{-1}
Gas constant	$R = N_A k$	8.314 47		$\text{J K}^{-1} \text{ mol}^{-1}$
		8.314 47	10^{-2}	$\text{dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$
		8.205 74	10^{-2}	$\text{dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$
		6.236 37	10	$\text{dm}^3 \text{ Torr K}^{-1} \text{ mol}^{-1}$
Planck's constant	h	6.626 08	10^{-34}	J s
	$\hbar = h/2\pi$	1.054 57	10^{-34}	J s
Avogadro's constant	N_A	6.022 14	10^{23}	mol^{-1}
Atomic mass constant	m_u	1.660 54	10^{-27}	kg
Mass				
electron	m_e	9.109 38	10^{-31}	kg
proton	m_p	1.672 62	10^{-27}	kg
neutron	m_n	1.674 93	10^{-27}	kg
Vacuum permittivity	$\epsilon_0 = 1/c^2 \mu_0$	8.854 19	10^{-12}	$\text{J}^{-1} \text{ C}^2 \text{ m}^{-1}$
	$4\pi e_0$	1.112 65	10^{-10}	$\text{J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Vacuum permeability	μ_0	4π	10^{-7}	$\text{J s}^2 \text{ C}^{-2} \text{ m}^{-1} (= \text{T}^2 \text{ J}^{-1} \text{ m}^3)$
Magneton				
Bohr	$\mu_B = e\hbar/2m_e$	9.274 01	10^{-24}	J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	5.050 78	10^{-27}	J T^{-1}
g value	g_e	2.002 32		
Bohr radius	$a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 35	10^{-3}	
	α^{-1}	1.370 36	10^2	
Second radiation constant	$c_2 = hc/k$	1.438 78	10^{-2}	m K
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3 c^2$	5.670 51	10^{-8}	$\text{W m}^{-2} \text{ K}^{-4}$
Rydberg constant	$R = m_e e^4/8h^3 c \epsilon_0^2$	1.097 37	10^5	cm^{-1}
Standard acceleration of free fall	g	9.806 65*		m s^{-2}
Gravitational constant	G	6.673	10^{-11}	$\text{N m}^2 \text{ kg}^{-2}$

*Exact value

The Greek alphabet

A, α	alpha	H, η	eta	N, ν	nu	Y, υ	upsilon
B, β	beta	Θ, θ	theta	Ξ, ξ	xi	Φ, ϕ	phi
Γ, γ	gamma	I, ι	iota	Π, π	pi	X, χ	chi
Δ, δ	delta	K, κ	kappa	P, ρ	rho	Ψ, ψ	psi
E, ϵ	epsilon	Λ, λ	lambda	Σ, σ	sigma	Ω, ω	omega
Z, ζ	zeta	M, μ	mu	T, τ	tau		