THE STRUCTURE OF PHYSICAL CHEMISTRY

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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. Its concepts are used to explain and interpret observations on the physical and chemical properties of matter. Physical chemistry is essential for developing and interpreting the techniques used to determine structure and properties, particularly spectroscopy and computational procedures, and their application to the development and understanding of modern materials and biologically important substances.

0.1 THE STRUCTURE OF SCIENCE

A scientific **law** is a summary of experience. Thus, we encounter the *laws of thermodynamics*, which are summaries of observations on the transformations of energy. Laws are often expressed mathematically, as in the **perfect gas law** (or *ideal gas law*):

$$\text{Perfect gas law: } pV = nRT \tag{1}$$

which is an approximate description of (an approximate 'equation of state' for) the physical properties of gases (with p the pressure, V the volume, n the amount, R a universal constant, and T the temperature). We also encounter the *laws of quantum mechanics*, which summarize observations on the behaviour of individual particles, such as molecules, atoms, and subatomic particles.

The first step in accounting for a law is to propose a **hypothesis**, which is essentially a guess at an explanation of the law in terms of more fundamental concepts. Dalton's *atomic hypothesis*, which was proposed to account for the laws of chemical composition and changes accompanying reactions, is an example. When a hypothesis has become established, perhaps as a result of the success of further experiments it has inspired or by a more elaborate formulation (often in terms of mathematics) that puts it into the context of broader aspects of science, it is promoted to the status of a **theory**. Among the theories we encounter are the theories of *chemical equilibrium*, *atomic structure*, and the *rates of reactions*.

A characteristic of physical chemistry (like other branches of science) is that to develop theories, it adopts models of the system it is seeking to describe. A **model** is a simplified version of the system that focuses on the essentials of the problem. Once a successful model has been constructed and tested against known observations and any experiments the model inspires, it can be made more sophisticated and incorporate some of the complications that the original model ignored. Thus, models provide the initial framework

for discussions, and reality is progressively captured rather like a building is completed, decorated, and furnished. One example is the **kinetic model** of gases, in which a perfect gas is regarded as a collection of non-interacting point-like particles in ceaseless, random motion. The kinetic model is elaborated by the inclusion of intermolecular interactions, and used to account for the properties of **real gases**, or actual gases. Another example is the **nuclear model** of an atom, and in particular a hydrogen atom, which is used as a basis for the discussion of the structures of all atoms. In the initial model, the interactions between electrons are ignored; to elaborate the model, repulsions between the electrons are taken into account progressively more accurately.

It is often convenient to preserve the form of equations developed on the basis of a simple model in any elaboration of the model. The advantage of such a procedure is that the appearance of many equations is then preserved and they remain familiar. Thus, an approximate description of chemical equilibrium is in terms of an equilibrium constant K_c for the reaction $A + B = C + D$ expressed in terms of molar concentrations [X]:

Equilibrium constant:

$$K_c = \frac{[C][D]}{[A][B]} \tag{2}$$

and its relations to the thermodynamic quantity known as the 'standard Gibbs energy of reaction' by the *approximate* expression

$$\Delta_r G^o = -RT \ln K_c \tag{3}$$

However, if the molar concentrations are replaced by the effective concentrations known as **activities**, a_X, and we define K as

Thermodynamic equilibrium constant: $\quad K = \dfrac{a_C a_D}{a_A a_B} \tag{4}$

then the thermodynamic expression

$$\Delta_r G^o = -RT \ln K \tag{5}$$

is exact. Physical chemistry helps to make this a practically useful procedure by establishing a relation between the effective concentration and the true concentration.

0.2 MATTER

Matter is anything tangible that has mass. Thus, gold and flesh are forms of matter, but electromagnetic radiation and justice are not. A more fundamental definition of matter is that

it is a collection of the fundamental particles known as fermions bound together by the fundamental particles known as bosons; for our more elementary purposes, we shall interpret this view as implying that matter is anything composed of atoms, which are collections of nuclei and electrons bound together by electrostatic interactions. A **substance** is a distinct, pure form of matter. Thus, of gold and flesh, only gold is a substance in the technical sense, for flesh is a mixture of many substances.

0.2(a) Measures of amount

The **amount of substance**, n (more colloquially 'number of moles' or 'chemical amount'), in a sample is reported as a multiple of the unit called a **mole** (mol). The formal definition of 1 mol is that it is the amount of substance that contains as many objects (atoms, molecules, ions, or other specified entities) as there are atoms in exactly 12 g of carbon-12. This number is found experimentally (by using mass spectrometry to determine the mass of a single atom of carbon-12 and dividing that mass into 12 g) to be approximately 6.02×10^{23}. The number of entities per mole is called **Avogadro's constant**, N_A, and its currently accepted value is

$$\text{Avogadro's constant:} \quad N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$$

Note that N_A is a quantity with units, not a pure number. The relation between number of entities and their chemical amount is

$$\text{Relation between number and amount:} \qquad N = nN_A \qquad (6)$$

A distinction is made in chemistry between extensive properties and intensive properties. An **extensive property** is a property that depends on the amount of substance in the sample. An **intensive property** is a property that is independent of the amount of substance in the sample. Two examples of extensive properties are mass and volume. Examples of intensive properties are temperature, mass density (mass divided by volume), and pressure.

A **molar quantity**, X_m, is the value of an extensive property, X, of the sample divided by the amount of substance present in the sample.

$$\text{Molar quantity:} \qquad X_m = \frac{X}{n} \qquad (7)$$

With the property X measured in the units X and n measured in moles, the units of X_m are $X \text{ mol}^{-1}$ (for example, the molar volume, V_m, is reported in $cm^3 \text{ mol}^{-1}$ if the volume, V, is reported in cm^3). A molar quantity is intensive because the value of an extensive property X is proportional to the amount of substance, n, so X_m is independent of the amount of substance in the sample. The one exception to the notation X_m is the **molar mass**, the mass per mole, which is denoted simply M. The *molar mass of an element* is the mass per mole of

the element's atoms. The *molar mass of a molecular compound* is the mass per mole of molecules, and the molar mass of an ionic compound is the *mass per mole of its formula units.* A *formula unit* is an assembly of ions corresponding to the chemical formula of the compound; so the formula unit NaCl consists of one Na^+ ion and one Cl^- ion. The names 'atomic weight' and 'molecular weight' are still widely used to denote the numerical value of the molar mass (that is, the numerical multiple of g mol^{-1} used to report the molar mass). Thus, because the molar mass of carbon (that is, of carbon atoms) is 12.01 g mol^{-1}, its atomic weight is 12.01. The molar masses of large molecules are often reported as multiples of the unofficial unit the *dalton,* Da, where 1 Da = 1 g mol^{-1} and its multiple, the kilodalton, 1 kDa = 10^3 g mol^{-1}.

One very useful relation involving the molar mass is its use to interpret the mass, *m*, of a sample in terms of the amount of substance present:

Relation between mass and amount: $\qquad n = \dfrac{m}{M}$ $\qquad\qquad\qquad$ (8)

0.2(b) Measures of concentration

'Concentration' is an indication of the density with which matter is packed into a region of space. The **molar concentration** (strictly, 'amount of substance concentration'; colloquially, 'molarity') of a solute in a solution, c_X or [X], refers to the amount of substance of the solute divided by the volume of the solution.

Molar concentration: $\qquad c_X \text{ or } [X] = \dfrac{n_X}{V_{solution}}$ $\qquad\qquad$ (9)

Molar concentration is usually expressed in moles per litre (mol L^{-1} or mol dm^{-3}; 1 L is identical to1 dm^3). A solution in which the molar concentration of the solute is 1 mol L^{-1} is prepared by dissolving 1 mol of the solute in sufficient solvent to prepare 1 L of solution. Such a solution is widely called a '1 molar solution' and denoted 1 M. The term **molality**, b_X, refers to the amount of substance of solute divided by the mass of solvent used to prepare the solution:

Molality: $\qquad b_X = \dfrac{n_X}{m_{solvent}}$ $\qquad\qquad\qquad$ (10)

The units of molality are typically moles of solute per kilogram of solvent (mol kg^{-1}).

The development of an appreciation of events on an atomic scale is a valuable talent in physical chemistry. In a 1 M NaCl(aq) solution, the average separation between oppositely charged ions is about 1 nm, which is enough to accommodate about three H_2O molecules. A dilute solution typically means a solution of molar concentration of no greater than about

$0.01\ mol\ L^{-1}$. In such solutions, the ions are separated by about 10 H_2O molecules.

0.3 ENERGY

The central concept of all explanations in physical chemistry, as in so many other branches of physical science, is that of **energy**, the capacity to do work (where 'work' means motion against an opposing force). We shall often make use of the universal law of nature

> *Conservation of energy:* the total energy of an isolated system is unchanged by any process

That is, energy can be neither created nor destroyed. Therefore, although energy can be transferred from one location to another (as when water in a beaker is heated by electricity generated in a power station), the total energy available is constant.

0.3(a) Contributions to the energy

There are two contributions to the the total energy of a system from the matter it contains, the kinetic energy and the potential energy. The total energy (the conserved quantity in an isolated system) is the sum of the two contributions.

The **kinetic energy**, E_K, is the energy a body possesses as a result of its motion. For a body of mass m travelling at a speed v, the kinetic energy is

Kinetic energy: $\qquad E_K = {}^1/_2\ mv^2$ $\qquad\qquad\qquad\qquad$ (11)

A heavy body travelling rapidly has a high kinetic energy. A stationary body has zero kinetic energy.

The **potential energy**, E_P or (when there is no fear of confusion with the symbol for volume) V, of a body is the energy it possesses as a result of its position. The zero of potential energy is arbitrary. For example, the gravitational potential energy of a body is often set to zero at the surface of the Earth; the electrical potential energy of two charged particles is set to zero when their separation is infinite. No universal expression for the potential energy can be given because it depends on the type of interaction experienced by the body. However, there are two common types of interaction that give rise to simple expressions. One is the potential energy of a body in the gravitational field close to the surface of the Earth (a gravitational field acts on the mass of a body). If a body of mass m is at a height h above the surface of the Earth, then its potential energy is

Gravitational potential energy (close to surface of the Earth): $\ E_P = mgh$ $\qquad$ (12)

where g is a constant called the **acceleration of free fall**. The 'standard value' of this

quantity, which in fact varies slightly with location and altitude, is

Acceleration of free fall: $g = 9.81 \text{ m s}^{-1}$

Note that $E_P = 0$ at $h = 0$ (the arbitrary zero mentioned previously). This expression is an approximation to the full expression for the gravitational potential energy of a body of mass m at a distance r from the centre of the Earth (or any other body) of mass m_E:

Gravitational potential energy (general):

$$E_P = -\frac{Gmm_E}{r} \tag{13}$$

Here G is the **gravitational constant**

Gravitational constant: $G = 6.673 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}$

This exact expression reduces to the approximate expression with $r = r_E + h$, where r_E is the radius of the Earth, $h \ll r_E$, and $g = Gm_E/r_E^2$.

Of greater importance in chemistry is the potential energy of a charged body in the vicinity of another charged body. If a particle (a point-like body) of charge q_1 is at a distance r in a vacuum from another particle of charge q_2, then their potential energy is given by the expression

Coulomb   potential   energy
$$E_P = \frac{q_1 q_2}{4\pi\varepsilon_0 r} \tag{14}$$

The constant ε_0 ('epsilon zero') is the **vacuum permittivity**, a fundamental constant with the value

Vacuum permittivity: $\varepsilon_0 = 8.854\ 19 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$

Note that, as remarked previously, $E_P = 0$ at infinite separation. This very important relation is called the **Coulomb potential energy** and the interaction it describes is called the **Coulomb interaction** of two charges. The Coulomb interaction is important in chemistry because we deal frequently with the interactions between the charges of electrons, nuclei, and ions.

0.4(b) Energy units

The SI unit of energy is the **joule** (J), which is defined as

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

A joule is quite a small unit of energy: for instance, each beat of the human heart consumes about1 J. The unit is named after the nineteenth-century scientist J.P. Joule, who helped to establish the role of energy in science. The **molar energy** is the total energy of a sample divided by the amount of substance; it is normally expressed in joules per mole (J mol^{-1}) or a multiple of this unit, most commonly kilojoules per mole (kJ mol^{-1}).

Although the joule is the SI unit of energy, it is sometimes convenient to employ other units. One of the most useful alternative energy units in chemistry is the **electronvolt** (eV): 1 eV is defined as the kinetic energy acquired when an electron is accelerated from rest through a potential difference of 1 V. The relation between electronvolts and joules is

Electronvolt: $1\text{ eV} = 1.602\ 176 \times 10^{-19}\text{ J}$

Many processes in chemistry involve energies of a few electronvolts. For example, to remove an electron from a sodium atom requires about 5 eV. Calories (cal) and kilocalories(kcal) are still encountered in the chemical literature. The original definition of the thermochemical calorie, $\text{cal}_{thermochem}$, was that it was the energy required to raise the temperature of 1 g of water at 14.5°C by 1°C. The calorie is now defined in terms of the joule:

Calorie: $1\text{ cal} = 4.184\text{ J (exactly)}$

0.4(c) Equipartition

A molecule has a certain number of degrees of freedom, such as its ability to *translate* (the motion of its centre of mass through space), *rotate* around its centre of mass, or *vibrate* (as its bond lengths and angles change). Many physical and chemical properties depend on the energy associated with each of these modes of motion. For instance, a chemical bond might break if a lot of energy becomes concentrated in it. The **equipartition theorem** is a useful guide to the average energy associated with each degree of freedom when the sample is at a thermodynamic ('absolute') temperature T. There are two parts to the theorem, one qualitative and the other quantitative.

The qualitative part of the theorem tells us that *all degrees of freedom have the same average energy*. That means 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, and each rotational degree of freedom also has the same energy. That is, in a normal sample, 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.

To introduce the quantitative part of the theorem we have to be more precise about what we mean by 'degree of freedom'. From now on, we shall refer to a 'quadratic term' in the energy, a term for the kinetic or potential energy that appears as the square of a coordinate

or a velocity (or momentum). For example, because the kinetic energy of a body of mass m free to move in three dimensions is

$$E_K = \tfrac{1}{2} m v_x^2 + \tfrac{1}{2} m v_y^2 + \tfrac{1}{2} m v_z^2 \tag{15}$$

there are three quadratic terms. The equipartition theorem then goes on to say that

The average energy associated with each quadratic term is equal to ½kT

where k is **Boltzmann's constant**

Boltzmann's constant: $k = 1.380\,65 \times 10^{-23}$ J K^{-1}

Boltzmann's constant is related to the gas constant by

Gas constant: $R = N_A k \tag{16}$

For instance, the average kinetic energy of a molecule free to move in three dimensions is $\tfrac{3}{2}kT$, as there are three quadratic contributions to the kinetic energy.

In passing, it should be noted that one reason why R occurs in so many formulas, including those apparently wholly unrelated to gases, is that it is really the fundamental constant k appearing in disguise (R is, in effect, the molar Boltzmann's constant). The quantity kT, which has the value 4×10^{-21} J (more briefly 4 zJ, where z, zepto, is the uncommon but useful SI prefix for 10^{-21}) at 25°C, or 26 meV, is an indication of the average energy carried by a mode of motion at a temperature T.

A very important point to acknowledge is that the equipartition theorem is derived from classical physics. The theorem is inapplicable when quantization is important (see below). Broadly speaking, we can be confident about using it for average translational motion in gases, guardedly confident about applying it to the rotation of most molecules, and not apply it to their vibrational motion.

0.4(d) The quantization of energy

The great revolution in physics that occurred in the opening decades of the twentieth century arising from the introduction of **quantum mechanics** is of crucial importance to chemistry. Chemistry is concerned with the behaviour of subatomic particles, particularly electrons in the presence of nuclei, and it is essential to use quantum mechanics when dealing with such small particles. The principal feature of quantum mechanics that distinguishes it from the **classical mechanics** of Newton and his immediate successors, is that *matter has a wavelike character*. That is, instead of particles and waves being distinct entities, particles have some of the properties of waves and waves have some of the properties of particles.

This wave–particle **duality,** the possession of the characteristics of both waves and particles, has a number of profoundly important consequence. For instance, if a particle has a linear momentum p (the product of mass and velocity, $p = mv$), then according to quantum mechanics it also has (in some sense) a wavelength λ (lambda), given by the **de Broglie relation**:

$$\text{de Broglie relation:} \qquad \lambda = \frac{h}{p} \qquad\qquad (17)$$

where h is **Planck's constant**,

$$\text{Planck's constant:} \qquad h = 6.626\ 08 \times 10^{-34} \text{ J s}$$

The wavelengths of macroscopic objects are so small (because their mass is so great) that it is wholly negligible. However, for particles with masses comparable to atoms and, even more, electrons, the wavelength is comparable to the dimensions of the region to which the particle is confined (for instance, the diameter of an atom), and it is essential to take the wave character into account both qualitatively and quantitatively.

A second consequence of wave–particle duality is that, provided the particle of interest is confined to a region of space (such as an atom), then its energy is **quantized**, or confined to certain discrete values. These permitted energies are called **energy levels** and their values depend on the characteristics of the particle (for instance, its mass) and the extent of the regions 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.

0.4(e) The energies of material objects

For particles in containers of macroscopic dimensions the separation of translational energy levels is so small that for all practical purposes their translational motion is unquantized and can be varied virtually continuously. That is not the case for the rotational and vibrational motion of molecules, nor for the energies of electron in atoms. The point to bear in mind is that the separation of energy levels is small for molecular rotational motion, larger for molecular vibrational motion, and greatest for the energies of electrons in atoms and molecules (Fig. 1). The separations of energy levels for a small molecule are about 10^{-23} J (0.01 zJ) for rotational motion (which corresponds to 0.01 kJ mol^{-1}), 10^{-20} J (10 zJ) for vibrational motion (10 kJ mol^{-1}), and 10^{-18} J (1 aJ, where a is another uncommon but useful SI prefix, standing for atto and denoting 10^{-18}) for electronic excitation (10^{3} kJ mol^{-1}).
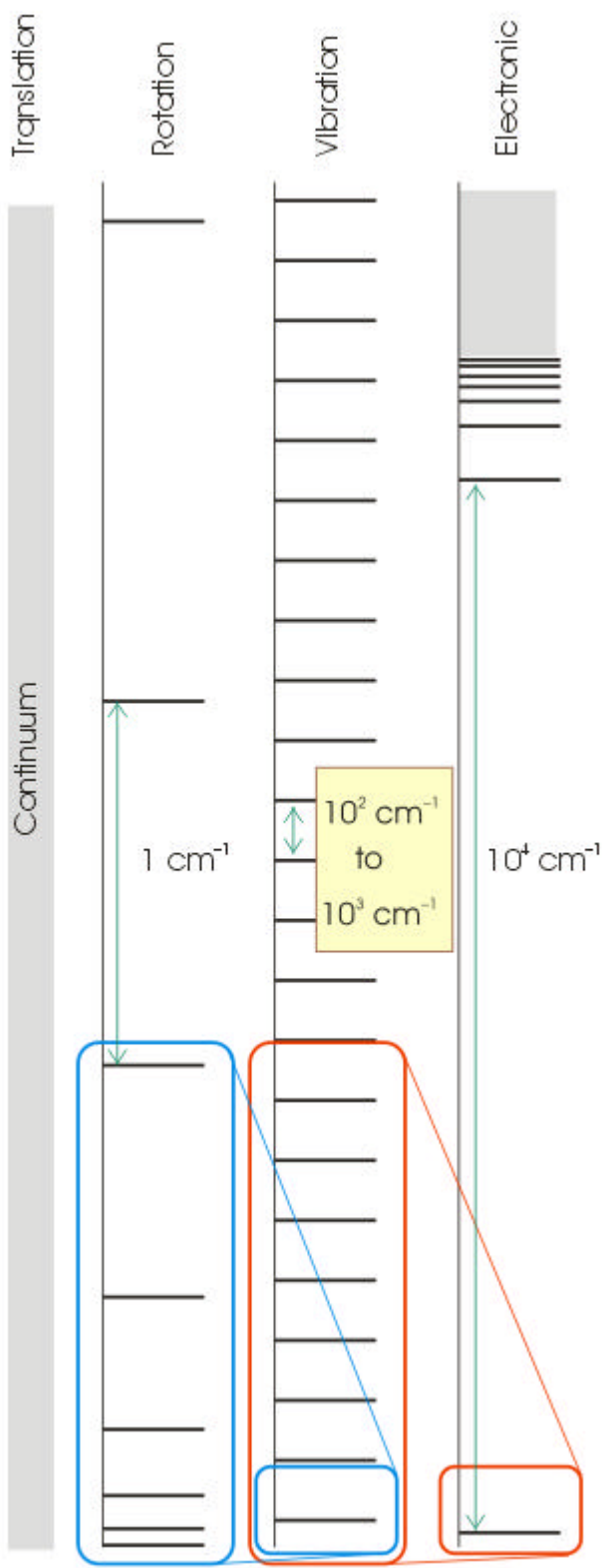
Figure 1 A representation of the quantization of the energy of different types of motion. Free translational motion in an infinite region is not quantized, and the permitted energy levels form a continuum. Rotation is quantized, and the separation increases as the state of excitation increases. The separation between levels depends on the moment of inertia of the molecule. Vibrational motion is quantized, but note the change in scale between the ladders. The separation of levels depends on the masses of atoms in the molecules and the rigidities of the bonds linking them. Electronic energy levels are quantized, and the separations are typically very large (of the order of 1 eV).
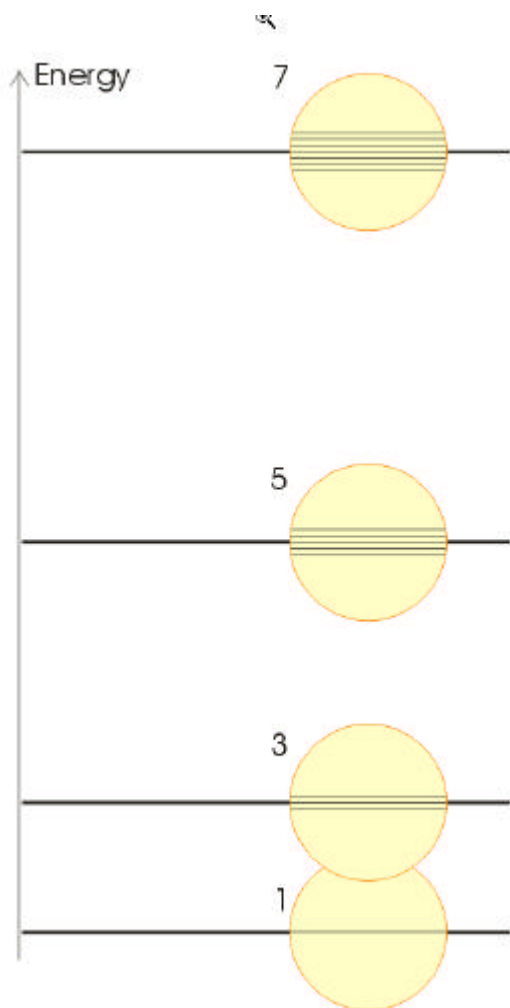
Figure 2 A single energy level might be composed of many individual states. Here we see how the degeneracy increases with energy for a rotating linear molecule.

A final point in this connection is that we need to be aware that more than one **state,** a specified condition of motion, can correspond to a given energy level. For example, a molecule can rotate in one plane at a certain energy, but it may also be able to rotate in a different plane with the same energy; each different mode of rotational motion corresponds to a distinct rotational state of the molecule. The number of individual states that belong to one energy level is called the **degeneracy** of that level (Fig. 2). If there is only one state of motion corresponding to a particular energy, then we say that the level is non-degenerate. The principles of quantum mechanics allow us to predict the degeneracy of each energy level. For instance, we find that although the lowest energy level of an electron in a hydrogen atom is non-degenerate, the next higher energy level is four-fold degenerate (that is, there are four states with the same energy).

0.4(f) The energy of the electromagnetic field

An **electromagnetic field** is an oscillating electric and magnetic disturbance that spreads as a wave through empty space, the vacuum. The wave travels at a constant speed called the **speed of light**, c,

Speed of light (in a vacuum): $c = 2.997\ 924\ 58 \times 10^8$ m s^{-1} (an exact, defined value)

As its name suggests, an electromagnetic field has two components, an **electric field** that acts on charged particles (whether stationary of moving) and a **magnetic field** that acts only on moving charged particles.

An electromagnetic field is characterized by a **wavelength**, λ, the distance between the neighbouring peaks of the wave, and its **frequency**, ν (nu), the number of times per second at which the field returns to its original value (Fig. 3). The frequency is measured in **hertz** (Hz):

Hertz: 1 Hz $= 1$ s^{-1}

and related to the wavelength by

Relation between wavelength and frequency: $\quad\quad \lambda\nu = c \quad\quad\quad\quad (18)$

This relation implies that the shorter the wavelength of the radiation, the higher its frequency.
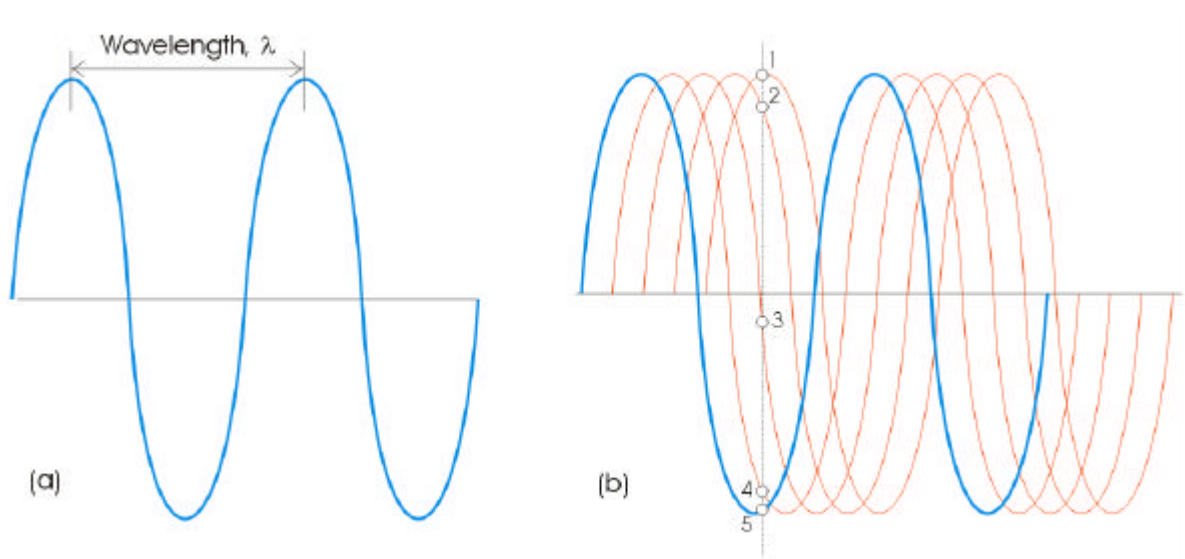

Figure 3 (a) The wavelength, λ, of a wave is the peak-to-peak distance. (b) The wave is shown travelling to the right at a speed c; at a given location, the instantaneous amplitude of the wave changes through a complete cycle (the dots numbered 1 to 5 show approximately half a cycle) as it passes a given point, and the frequency, ν, is the number of cycles per second that occur at a given point.

The characteristics of a wave are also reported by giving the **wavenumber**, $\tilde{\nu}$ ('nu tilde'), of the radiation, where

$$\text{Wavenumber:} \qquad \tilde{\nu} = \frac{1}{\lambda} \qquad\qquad (19)$$

The 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 here are 5 complete wavelengths in 1 cm. In a vacuum, when the radiation is moving at a speed c, this definition is equivalent to

$$\text{Vacuum wavenumber:} \qquad \tilde{\nu} = \frac{\nu}{c} \qquad\qquad (20)$$

The classification of the electromagnetic field according to its frequency and wavelength is summarized in Fig. 4.
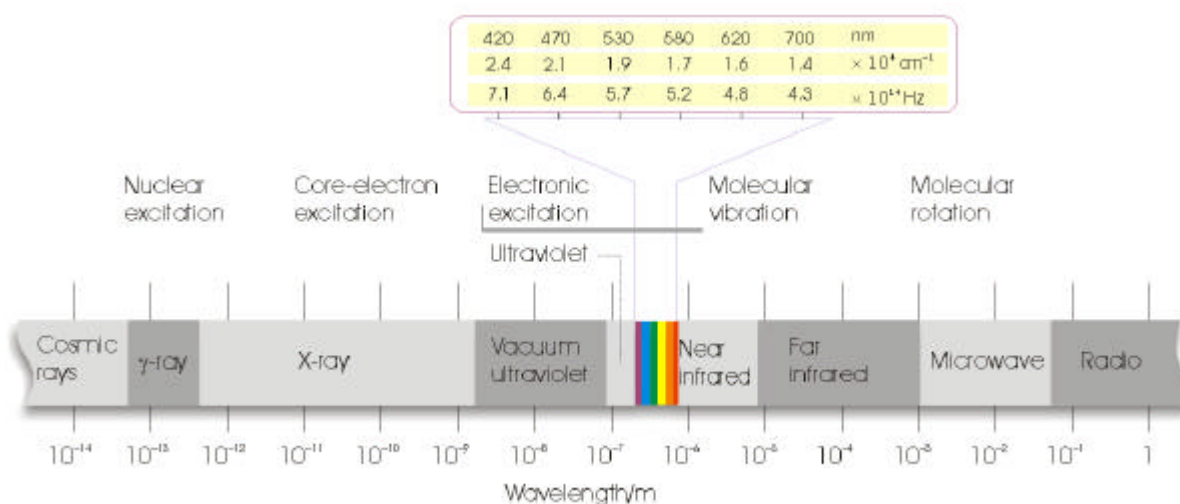

Figure 4 The electromagnetic spectrum and the classification of the spectral regions.

Quantum mechanics adds to this wave-like description of electromagnetic radiation by introducing the concept of particle-like packets of electromagnetic energy called **photons**. The energy of each photon is determined by its frequency í, by

$$\text{Photon energy:} \qquad E = h\nu \qquad\qquad (21)$$

This relation implies that photons of microwave radiation have lower energy than photons of visible light (which consists of shorter wavelength, higher frequency radiation). It also implies that the energies of photons of visible light increase as the light is changed from red (longer wavelength) to violet (shorter wavelength). It is useful to note that the relations $E = h\nu$ and $\nu = c\tilde{\nu}$ can be combined to express energies as wavenumbers; it turns out, for instance, that

$$1 \text{ eV} = 8066 \text{ cm}^{-1}$$

The **intensity** of the radiation is determined by the number of photons in the ray: an intense ray consists of a large number of photons; a feeble ray consists of only a few photons. A retinal cell in the human eye can respond to a single photon; a lamp rated at 100 W (where 1 W = 1 J s^{-1}; W denotes the watt) generates about 10^{19} photons each second, but even so takes several hours to generate 1 mol of photons.

0.4(g) The populations of states

The continuous thermal agitation that the molecules experience in a sample at $T > 0$ ensures that they are distributed over the available energy levels. One particular molecule may be in one low energy state 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. 5). Nevertheless, whatever the temperature, there is always a higher
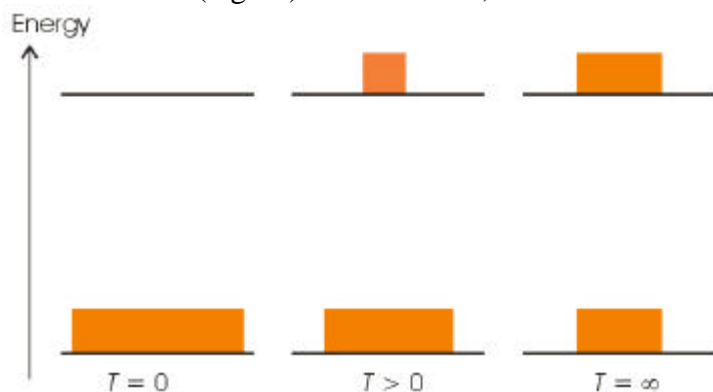
Figure 5 The population of states in a two-level system (with each level non-degenerate) at three different temperatures. At $T = 0$ the entire population is in the lower state; at infinite temperature, the populations are equal.

population in a state of low energy than one of high energy. The only exception occurs when the temperature is infinite: then all states of the system are equally populated. This condition is unattainable in practice. The formula for calculating the populations of states of various energies is called the **Boltzmann distribution** and was derived by the Austrian scientist Ludwig Boltzmann towards the end of the nineteenth century. This formula gives the ratio of the numbers of particles in states with energies E_i and E_j as

$$\text{Boltzmann distribution:} \qquad \frac{N_i}{N_j} = e^{-(E_i - E_j)/kT} \qquad\qquad (22)$$

We see that an interpretation of the **temperature** of a system is that it is the single parameter that controls the relative populations of the available states of the system..

An important point concerning the interpretation of the Boltzmann distribution is that it refers to the populations of *states*, not levels. Because the Boltzmann distribution refers to states, all the members of a degenerate set of states will have the same population. We shall see a consequence of this feature shortly. A typical energy separation between the ground state and the first electronically excited state of an atom or molecule is about 3 eV, which corresponds to 300 kJ mol^{-1}. In a sample at 25°C (298 K) the ratio of the populations of the two states is about e^{-121}, or about 10^{-53}. Therefore, essentially every atom or molecule in a sample is in its electronic ground state. The population of the upper state rises to about 1 per cent of the population of the ground state only when the temperature reaches 10^4 °C. The separation of vibrational energy levels is very much less than that of electronic energy levels (about 0.1 eV, corresponding to 10 kJ mol^{-1}), but nevertheless at room temperature only the lowest energy level is significantly populated. Only about 1 in e^4, or about 60, molecules is not in its ground state. Rotational energy levels are much more closely spaced than vibrational energy levels (typically, about 100 to 1000 times closer), and even at room temperature we can expect many rotational states to be occupied. Therefore, when considering the contribution of rotational motion to the properties of a sample, we need to take into account the fact that molecules occupy a wide range of different states, with some rotating rapidly and others slowly.

The important features of the Boltzmann distribution to bear in mind are that the distribution of populations is an exponential function of energy and temperature, and that more states 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). Moreover, more states are occupied at high temperatures than at low temperatures.

Figure 6 summarizes the form of the Boltzmann distribution for some typical sets of energy levels.

The Boltzmann distribution takes a special form when we consider the free translational motion of noninteracting gas molecules. Different energies now correspond to different speeds (because the kinetic energy is equal to $\frac{1}{2}mv^2$, so the Boltzmann formula can
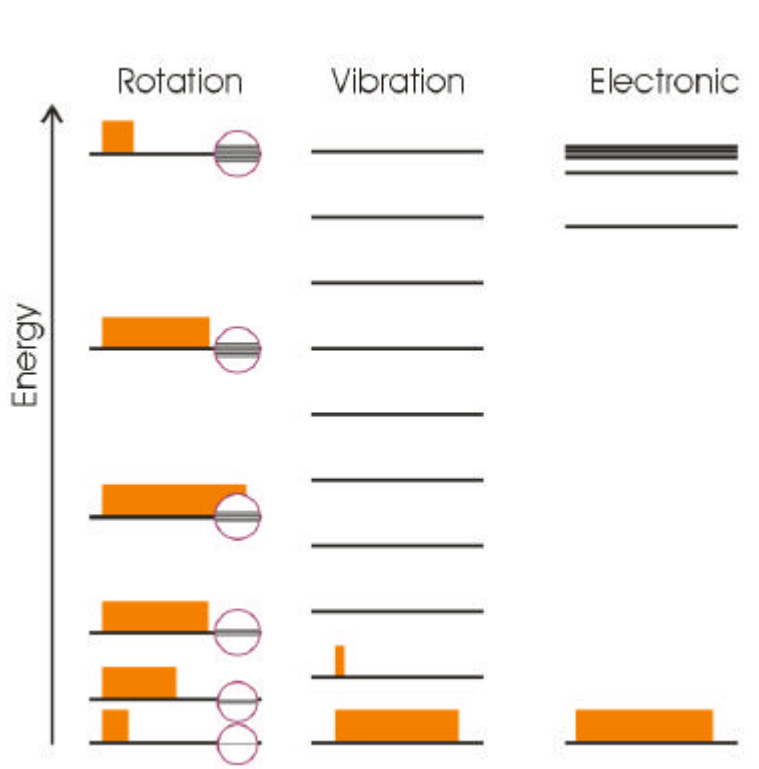
Figure 6 The Boltzmann distribution for three types of motion at a single temperature. There is a change in scale between the three stacks of levels (recall Fig. 1). Only the ground electronic state is populated at room temperature in most systems, and the bulk of the molecules are also in their ground vibrational state. Many rotational states are populated at room temperature as the energy levels are so close. The peculiar shape of the distribution over rotational states arises from the fact that each energy level actually corresponds to a number of degenerate states in which the molecule is rotating at the same speed but in different orientations. Each of these states is populated according to the Boltzmann distribution, and the shape of the distribution reflects the total population of each level.

be used to predict the proportions of molecules having a specific speed at a particular temperature. The expression giving the proportion of molecules $f(v)$ that have a particular speed v is called the **Maxwell distribution**, and has the features summarized in Fig. 7:

$$\text{Maxwell distribution:} \qquad f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT} \qquad (23)$$

where M is the molar mass. The bulge in the distribution represents the fact the kinetic energy
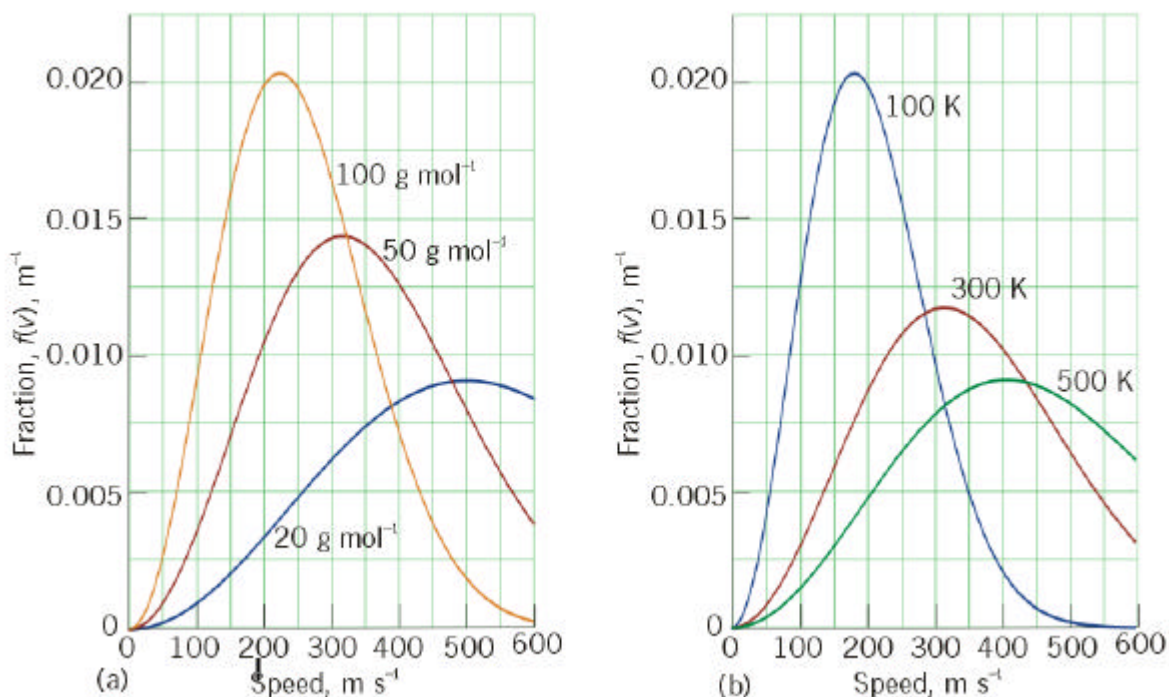
Figure 8 The essential content of the Maxwell distribution of molecular speeds is summarized by these two diagrams. (a) The distribution of speeds for molecules with different masses at the same temperature. (b) The distribution of speeds for a given species of molecule at different temperatures.

of a molecule depends on its speed, and there are many ways of obtaining a given value of the speed v with different values of the components v_x, v_y, and v_z relative to the three axes, particularly when the speed is high. In other words, translational energy levels are highly degenerate, and the degeneracy increases with energy. Therefore, although the populations of individual states decrease with increasing energy (and hence speed), there are many more states of a given energy at high energies and the product of this rising degeneracy and the falling exponential function has a bulge at an intermediate energy. Notice how 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.

The speed corresponding to the maximum in the graph is the **most probable speed**, the speed most likely to be found for a molecule selected at random. The illustration also shows how the distribution varies with mass for some components of air at 25°C. The lighter molecules move, on average, much faster than the heavier ones.

0.3 THE COMPONENTS OF PHYSICAL CHEMISTRY

The text is divided into three major parts, but the boundaries are not rigid and each part draws heavily on the others. For convenience, we have labelled the parts *Equilibrium*, *Structure*, and *Change*.

The section entitled *Equilibrium* deals largely with **thermodynamics**, the study of the transformations of energy and the relations between the bulk properties of matter. Thermodynamics is summarized by a number of laws, two of which take centre stage. The **First Law** is an elaboration of the law of the conservation of energy, which takes into account the fact that energy may be transferred from one system to another by the agencies of heat as well as work. The chemical application of the First Law is called **thermochemistry**, and is used principally to study the heat released or required by chemical reactions. The **Second Law** introduces the concept of **entropy** and is used to account for the direction of natural change. The application of the Second Law to chemical phenomena is simplified by the introduction of the **Gibbs energy** of a system and the closely related **chemical potential** of a substance. These quantities allow us to account for the natural direction of physical and chemical change and, in particular, the condition of **chemical equilibrium**, when a reaction mixture has no further tendency to undergo change.

The section entitled *Structure* is based on quantum mechanics. It starts with the **structures of atoms and molecules** and descriptions of the **chemical bond**. One of the most powerful ways to identify molecules in a sample, and the allowed energy levels, is through **spectroscopy**, and this section explores the information that can be obtained from techniques that involve increasingly large transfers of energy between molecules and the electromagnetic field. **Nuclear magnetic resonance** is a very important spectroscopic technique used in routine laboratory work and in medical diagnostics. Once the energy levels of molecules are known, a bridge can be built from these molecular properties to the properties of bulk systems treated by thermodynamics: the bridge is provided by **statistical thermodynamics**. This important topic provides techniques for calculating bulk properties, and in particular equilibrium constants, from molecular data. The section ends with a discussion of macromolecules and the solid state. For example, we see how the **X-ray diffraction** technique, which can be used to determine the three-dimensional arrangement of atoms in powders and crystals, plays a central role in materials science and molecular biology.

The section on *Change* is concerned with **chemical kinetics**, the study of the rates of chemical reactions. To understand the molecular mechanism of change, we need to understand how molecules move, either in free flight in gases or by diffusion through liquids: this is the domain of the **kinetic theory of gases** and the **diffusion equation**. Then we establish how the rates of reactions may be determined and expressed in terms of **rate laws** and explore how these rate laws give insight into the molecular processes by which chemical reactions occur. For the latter, we introduce techniques of increasing theoretical sophistication, including **collision theory**, **activated complex theory**, and—most detailed of all—**molecular reaction dynamics**. The account concludes with a discussion of two important classes of chemical reactions, those occurring at surfaces, which is essentially the

domain of **catalysis**, and those occurring at electrodes, the domain of **dynamic electrochemistry**.

The thrust of modern physical chemistry is towards the elucidation of complex problems in environmental science, materials science, and molecular biology. To understand these important domains of enquiry, ever more sophisticated techniques of investigation have to be introduced, which include the experimental techniques of spectroscopy, diffraction, and microscopy and the theoretical techniques implemented on computers but based on quantum mechanics and statistical thermodynamics. Physical chemistry provides new techniques of investigation and underpins the whole of the interpretational structure of chemistry.